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An Investigation of Photochemically Induced Reactions in a Chlorine-Ozone System

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AN INVESTIGATION OF PHOTOCHEMICALLY INDUCED REACTIONS IN A CHLORINE-OZONE SYSTEM

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TABLE OF CONTENTS

SUMMARY

Photochemically induced reactions between chlorine (Cl_2) and ozone (O_3) were studied in a glass reactor at constant temperature. Light of wavelength 365-366.5 nm. was used to initiate the reactions by the following process:

$$Cl_2(^1\Sigma_g^+) + h\nu \longrightarrow Cl_2(^3\pi_{o+u}) \rightarrow Cl(^2P_{3/2}) + Cl(^2P_{1/2}).$$

The reactions were run with steady illumination for periods up to 26 hours after which the products of the subsequent series of thermal reactions were dissolved in water. The resultant solutions were analyzed by various colorimetric techniques for the presence of chloride (Cl^-), hypochlorite (ClO^-), chlorite (ClO_2^-), chlorate (ClO_3^-), and perchlorate (ClO_4^-). This analysis showed that perchlorate was the only ionic chlorine species found which could be associated with a chlorine oxide product of the reaction system. Therefore, since dichlorine heptoxide (Cl_2O_7) is the anhydride of perchloric acid, dichlorine heptoxide was assumed to be the only product of the reaction system which was formed in detectable amounts. Two chlorine oxides, chlorine dioxide (ClO_2) and chlorine trioxide (ClO_3), were assumed to be present but at concentrations below a detectable level.

Under experimental conditions where chlorine, ozone, and diluent were at an initial concentration of 8.82×10^{-3} moles/liter and the light intensity was 3.05×10^{15} quanta/sec., the formation of dichlorine heptoxide was directly proportional to the absorbed light intensity, independent of temperature, slightly affected by the species of diluent, and approaching an apparent zero order with respect to ozone. Formation of dichlorine heptoxide proceeded with a small pressure increase. The average rate of formation of dichlorine heptoxide and the subsequent quantum yield over a 10-hour period were dependent on the species of diluent; with no diluent these values were 1.31×10^{-8} moles/liter sec. and 0.401; with helium (He) as diluent they were 1.16×10^{-8}

moles/liter sec. and 0.356; and with oxygen (O_2) as diluent they were 1.09×10^{-8} moles/liter sec. and 0.332.

Based on the data obtained in this study and that presented in the literature, a reaction mechanism is proposed. The mechanism consists of the primary process as shown above and eight secondary thermal reactions, six which lead to formation of dichlorine heptoxide and eight which decompose ozone. Also included in the mechanism are seven side reactions, four of which lead to chlorine atom recombination and three which account for chlorine monoxide (ClO) decomposition to oxygen and chlorine. The key reaction in the proposed mechanism is the formation of an ozone-chlorine atom complex (ClOOO) which can either decompose to ClO and oxygen or be somewhat stabilized by collision with a third body. The formation of ClO leads to a possible chain decomposition of ozone. The stabilized ClOOO complex is the starting point for stepwise nonchain formation of dichlorine heptoxide, where the ClOOO reacts with ozone to form chlorine dioxide which reacts further with ozone to form chlorine trioxide. The chlorine trioxide reacts with ozone to form a somewhat stabilized complex and/or a chlorine tetroxide radical (ClO_4), either of which reacts with chlorine trioxide to form dichlorine heptoxide.

The mechanism was manipulated using the steady state assumption for chlorine oxide intermediates. The resultant rate and quantum yield expressions for dichlorine heptoxide formation and ozone decomposition followed the requirements set up by this work and earlier work on the system. Using the results obtained in the present study and a number of applicable rate constants found in the literature, the rate constants for three of the unknown reactions were estimated. These three reactions involved the stabilization of the ClOOO complex. The estimated rate constant becomes a measure of the ability of the third body in question to achieve stabilization.

$$Cl + O_3 + M' \rightarrow ClOOO + M'; \quad k = 2.2 \times 10^4 \text{ liter}^2/\text{mole}^2\text{sec.}$$

$$Cl + O_3 + O_3 \rightarrow ClOOO + O_2; \quad k = 5.0 \times 10^4 \text{ liter}^2/\text{mole}^2\text{sec.}$$

$$Cl + O_3 + He \rightarrow ClOOO + He; \quad k < 1.0 \times 10^2 \text{ liter}^2/\text{mole}^2\text{sec.}$$

M' is the sum of the concentration of chlorine and ozone in the system, and the rate constant given is only applicable if the ratio of chlorine to ozone is one.

INTRODUCTION

Chlorine (Cl_2), oxygen (O_2), and chlorine dioxide (ClO_2) are compounds now used in the paper industry for the bleaching of wood pulp. Studies are now under way evaluating the bleaching ability of ozone (O_3) (1) and dichlorine monoxide (Cl_2O) (2). The paper industry is very zealous in its pursuit and evaluation of new bleaching agents. However, it seems to ignore the fundamental chemical and physical properties of these agents. Very little work has been done within the industry on the characterization of chlorine dioxide, other than establishing economical and safe means of use.

Chlorine dioxide is one of a number of chlorine oxide compounds. These compounds are interrelated in that they undergo many reactions with each other and transformations into each other. A thorough study of this class of compounds would aid in understanding these interrelations, with a possible benefit of indicating preparative schemes that are less costly than those now used. A photochemical system involving chlorine and ozone can be used to form a number of these oxides. The reported work is a study of this system.

The specific thesis objectives will be presented after a review of the existing literature.

LITERATURE REVIEW

This section gives general background knowledge of what has already been established concerning photochemically activated ozone-chlorine systems. The works of those who have directly studied the system will be presented along with their subsequent conclusions and the means through which these conclusions were made. The products found in the system will be stressed along with the possible intermediary compounds. Work on chlorine-oxygen systems and on individual reactions of the ozone-chlorine system will be presented. For more extensive understanding of the chlorine oxides and their interrelated systems, reviews by Mellor (3), Farrar (4), Schmeisser and Brandle (5), and Eachus (6) are recommended.

The system to be studied consists of mixtures of chlorine and ozone enclosed in a glass reactor under controlled temperature. The initiation of the reaction is made through irradiation by light which can be absorbed by either ozone to form molecular oxygen and atomic oxygen (O) or by chlorine to split the chlorine molecule into atoms (Cl). The system to be considered uses light of wavelength 365-366.5 nm. to split the chlorine molecule.

REVIEW OF PHOTOCHEMICAL TERMS

A review of some photochemical terms is given here to help facilitate understanding of the following sections. More intensive reviews can be found in any photochemical text. The vocabulary of photochemistry can be found in Pitts, et al. (7) while Calvert and Pitts (8) give intensive coverage to the subject.

PRIMARY PHOTOCHEMICAL PROCESS

A primary photochemical process is a process starting with the absorption of a quantum of light by a molecule and ending with the disappearance of the molecule or the molecule returning to its original state.

SECONDARY THERMAL PROCESS

A secondary thermal process is a thermal reaction initiated by free radicals or excited molecules produced in the primary process.

QUANTUM YIELD

The quantum yield is a measure of the ability of light of a specific wavelength to produce a certain product, or destroy a specific substance. It is the ratio of the number of molecules of a substance formed or destroyed to the number of quanta of light of the specified wavelength absorbed.

FLASH PHOTOLYSIS

Flash photolysis is the use of high intensity flashes of light to study a photochemical reaction; this is in comparison to the use of a relatively low intensity, steady light source.

BEER'S LAW

Beer's law is the relationship between the intensity of monochromatic light, I, transmitted by an absorbing medium, and the incident light, I_o, upon the medium,

$$I = I_o \, 10^{-\varepsilon bc}, \qquad (1)$$

where $\underline{b}$ = the path length, cm.;

$\underline{c}$ = the concentration, moles/liter; and

ε = the molar extinction coefficient, liters/mole cm.

The molar extinction coefficient is a function of wavelength.

ABSORBANCE

Absorbance is the value of $\log_{10} \underline{I_o}/\underline{I}$ at a given wavelength. It is also referred to as the optical density.

TRANSMITTANCE

Transmittance is the ratio of the intensity of the transmitted light to the incident light, $\underline{T} = \underline{I}/\underline{I_o}$.

ABSORBED LIGHT INTENSITY

The absorbed light intensity is represented by the symbol, $\underline{I_{abs}}$, and is found from the incident light intensity and transmitted light intensity, $\underline{I_{abs}} = \underline{I_o} - \underline{I}$.

MEASUREMENT OF LIGHT INTENSITY

Three means are used to measure light intensity: (1) a properly calibrated thermopile-galvanometer system, (2) chemical actinometry, where a previously calibrated chemical reaction is used, and (3) phototubes which measure relative light intensity.

MEDIUM PRESSURE LAMP

A medium pressure lamp is a type of Hg arc lamp which operates under a pressure of about 1 atm. The spectrum of the lamp gives a large number of

wavelengths which can be easily separated into near monochromatic light by the proper optical filters.

OPTICAL TRAIN

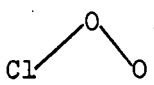
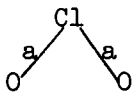
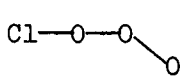
The optical train is the system of light source, apertures, lenses, and optical filters which is used to render a light beam columnar and monochromatic.

RELATIONSHIP BETWEEN CHLORINE TRIOXIDE AND DICHLORINE HEXOXIDE

Dichlorine hexoxide (Cl_2O_6) is the dimer of chlorine trioxide (ClO_3). The relationship of these two compounds is such that chlorine trioxide exists in the gaseous state with no dichlorine hexoxide, while in the liquid and solid states an equilibrium exists which is predominantly dichlorine hexoxide (9). For this reason, when chlorine trioxide is spoken of in later sections the gaseous state is being considered, while when dichlorine hexoxide is spoken of the liquid state is being considered. To aid in the following discussions, the name, formula, and structure of compounds important to the study are given in Table I.

TABLE I

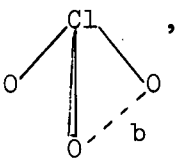
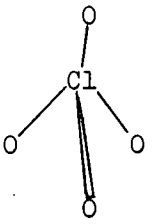
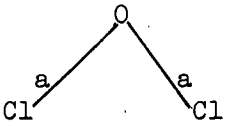
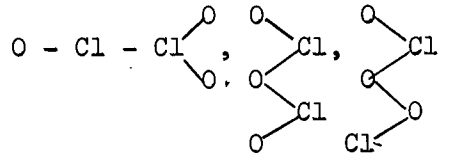
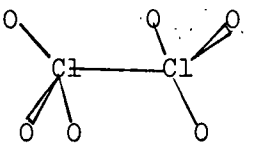
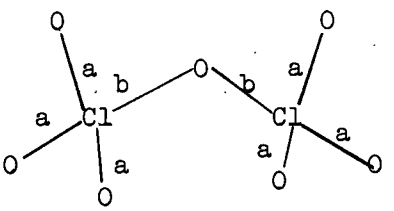
NAME, FORMULA, AND STRUCTURE OF IMPORTANT COMPOUNDS

Chemical Name	Formula	Structure	Reference
Chlorine monoxide	ClO	Cl —(a)— O, a = 1.546 A.	(14)
Chlorine peroxide	ClOO	 , <ClOO = 110-115°	(6,15)[a]
Chlorine dioxide	ClO_2	 , a = 1.49 A. <OClO = 118.5°	(16)
Chlorine atom-ozone complex	ClOOO		suggested structure

See end of table for footnotes.

TABLE I (Continued)

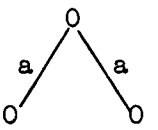
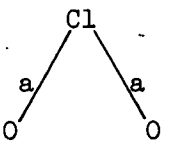
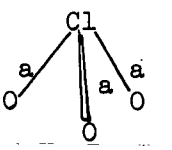
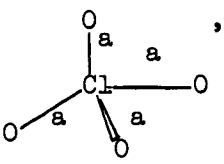
NAME, FORMULA, AND STRUCTURE OF IMPORTANT COMPOUNDS

Chemical Name	Formula	Structure	Reference
Chlorine trioxide	ClO_3	 , <OClO = 111° <OClO = 89° b = 2.243 A.	(17,18,19)[b]
Chlorine tetroxide	ClO_4		(20)[c]
Chlorine molecule	Cl_2	Cl —(a)— Cl, a = 1.988 A.	(21)
Dichlorine monoxide	Cl_2O	 a = 1.70 ± 0.02 A. <ClOCl = 110.8 ± 1.0°	(22)
Dichlorine dioxide	Cl_2O_2	ClO - - - ClO	(6)
Dichlorine trioxide	Cl_2O_3		(23,6)[d]
Dichlorine hexoxide	Cl_2O_6		(9)
Dichlorine heptoxide	Cl_2O_7	 a = 1.42 ± 0.01 A. b = 1.72 ± 0.03 A. <ab = 97 ± 3° <bb = 115 ± 5°	(24)
Triatomic chlorine	Cl_3	Cl - Cl - Cl	(25)[e]

See end of table for footnotes.

TABLE I (Continued)

NAME, FORMULA, AND STRUCTURE OF IMPORTANT COMPOUNDS

Chemical Name	Formula	Structure	Reference
Oxygen molecule	O_2	O —a— O, a = 1.20741 ± 0.00002 A.	(26)
Ozone	O_3	 , a = 1.278 ± 0.002 A. <OOO = 116.8 ± 0.5°	(27)
Hypochlorite	ClO^-	Cl ——— O	assumed
Chlorite	ClO_2^-	 a = 1.57 ± 0.03 A. <OClO = 110.5 ± 1.4°	(28)[f]
Chlorate	ClO_3^-	 , a = 1.57 A. <OClO = 106.7°	(29)[g]
Perchlorate	ClO_4^-	 , a = 1.43 A. <OClO = 109°	(30)[h]

[a] Angle calculated by (6) from suggestions of (15).
[b] Pyramidal shape suggested by (17), angle 111° given by (18), and angle 89° and
[c] distance 2.243 A. given by (19).
[c] This reference, (20), claims observation of ClO_4; it is assumed that this is
[d] the structure.
[d] Ref. (23) suggested first structure while Ref. (6) suggested last two.
[e] Observation of Cl_3 claimed by (25); structure assumed.
[f] Found in crystallographic study of NH_4ClO_2.
[g] Found in crystallographic study of $Ba(ClO_3)_2 \cdot H_2O$.
[h] Found in crystallographic study of $HClO_4 \cdot H_2O$.

PREVIOUS STUDIES OF THE CHLORINE-OZONE SYSTEM

The first study of the chlorine-ozone photochemical system was made in 1907 by Weigert (10). He used light absorbed by chlorine to initiate the reaction. Assuming that the net reaction was $2\ O_3 \longrightarrow 3\ O_2$, the reaction was monitored by a manometer. Weigert found that under the conditions used (1 atm. total pressure, 0.5-5% O_3, 5-70% Cl_2), the rate of decomposition of ozone was zero order with respect to ozone and proportional to the light absorbed. An interesting feature was that just before complete decomposition of ozone there was a rapid increase in the rate. Bonhoeffer (11) confirmed these results and reported a quantum yield of 2.0 ± 0.2 for the destruction of ozone. Bodenstein, Harteck, and Padelt (12) reported that dichlorine hexoxide is formed in the system when illuminated by red light, 620 nm., which activates ozone but not by blue light, which activates chlorine. Allmand (13) in 1926 suggested a mechanism for the system which was based on activated chlorine (Cl_2*) and oxygen (O_2*) molecules.

$$Cl_2 + h\nu \longrightarrow Cl_2^* \qquad (2)$$

$$Cl_2^* + O_3 \longrightarrow Cl_2 + O_2 + O + \text{energy} \qquad (3)$$

$$Cl_2^* + O_2 \longrightarrow Cl_2 + O_2^* \qquad (4)$$

$$O_2^* + O_3 \longrightarrow 2\ O_2 + O + \text{energy} \qquad (5)$$

$$Cl_2^* \longrightarrow Cl_2 + \text{energy} \qquad (6)$$

$$O_2^* \longrightarrow O_2 + \text{energy}. \qquad (7)$$

This mechanism is erroneous because it has been shown that chlorine upon absorption of light of wavelength 270-478 nm. dissociates into chlorine atoms (8). There is also no provision for intermediate chlorine oxides because at that time, 1926, it was felt that the ozone was completely decomposed to oxygen.

Equations (3) and (5) are interesting since they come close to describing the first step in the thermal decomposition of ozone, where ozone is struck by an inert body and is decomposed to oxygen, and an oxygen atom (31).

Bodenstein and Schumacher (32) presented the following mechanism which was based on the ozone molecule becoming activated (O_3^*) by light of wavelength 470 nm.

$$O_3 + h\nu \longrightarrow O_3^* \qquad (8)$$

$$O_3^* + Cl_2 \longrightarrow ClO + ClO_2 \qquad (9)$$

$$ClO_2 + O_3 \longrightarrow ClO_3 + O_2 \qquad (10)$$

$$ClO_3 + O_3 \longrightarrow ClO_2 + 2\,O_2 \qquad (11)$$

$$ClO_3 + ClO_3 \longrightarrow Cl_2 + 3\,O_2 \qquad (12)$$

$$2\,ClO_3 \longrightarrow Cl_2O_6 \qquad (13)$$

$$ClO + ClO \longrightarrow Cl_2 + O_2. \qquad (14)$$

Bodenstein and Schumacher suggested that Equation (13) occurred more readily at temperatures of 0 to 10°C., while Equation (12) occurred predominantly at higher temperatures. This mechanism is very similar to that proposed by Bodenstein, Padelt, and Schumacher (33) for the thermal reaction between chlorine and ozone at 35 and 50°C. In the thermal mechanism, Equations (8) and (9) are replaced by Equation (15).

$$Cl_2 + O_3 \longrightarrow ClO + ClO_2, \qquad (15)$$

and Equation (13) is eliminated. These two mechanism are characterized by the key step of formation of chlorine dioxide. All of the equations in this mechanism seem to be in doubt except Equations (10), (11), and (13). More recent work, as reviewed by Leighton (34), has shown that Equation (8) would more properly be written in the following manner:

$$O_3(S_o) + h\nu \longrightarrow O_3(T_1) \longrightarrow O_2(^3\Sigma_g^-) + O(^3P). \qquad (16)$$

For Equation (9) to occur it would require excessive atomic rearrangement. Equation (12) also would require excessive atomic rearrangement and, as suggested later in this section, the decomposition of chlorine trioxide occurs with initial formation of chlorine dioxide which then decomposes further in a complex manner. The term excessive atomic rearrangement will be used to describe those proposed reactions which do not appear feasible if carried out in one step. For example, if Equation (12) is to occur, as written, six chlorine-oxygen bonds must be broken. The energy required for this to occur would prohibit the reaction. Equation (14) is erroneous in light of recent work (35) on the breakdown of chlorine monoxide (ClO). Equation (15) also appears to require excessive atomic rearrangement. Equation (10) is accepted because it is a common preparative method for chlorine trioxide. Equation (11) is accepted because it is feasible in that it does not require excessive atomic rearrangement to occur. Equation (13) is the dimerization of chlorine trioxide which was discussed previously.

Allmand and Spinks (36) did a study of the reaction using light of wavelength 365 nm. Because their gases were somewhat wet they observed a film formed in the reactor. When the film was dissolved in water and tested qualitatively they got positive evidence for chlorate (ClO_3^-) and perchlorate (ClO_4^-) ion. Since dichlorine hexoxide dissolves in water to form chlorate and perchlorate ions, they concluded that chlorine trioxide was an intermediate in the reaction. They suggested the following mechanism:

$$Cl_2 + h\nu \longrightarrow 2\ Cl \qquad (17)$$

$$Cl + O_3 \longrightarrow ClO_3 \qquad (18)$$

$$2\ ClO_3 \longrightarrow Cl_2O_6 \qquad (13)$$

$$Cl + O_2 \longrightarrow ClO_2 \qquad (19)$$

$$ClO_2 + O_3 \longrightarrow ClO_3 + O_2. \qquad (10)$$

Equations (17), (13), and (10) are acceptable as written. However, Equation (18) is questionable since it requires excessive atomic rearrangement and Equation (19) is simply erroneous because recent work (35) has shown that the product of this reaction in the presence of a third body is chlorine peroxide (ClOO).

Allmand and Spinks (37,38) further studied the system using pressure measurements at wavelengths of 313, 365, and 420 nm., with high and low ozone concentrations, one atmosphere total pressure, and temperatures of 20, 25, and 30°C. For low ozone concentrations (less than 7%) the following results were reported. The rate of pressure increase is zero order with respect to ozone. Using 365 nm. wavelength light, at chlorine concentrations greater than 2-3%, the rate of pressure increase is proportional to light absorbed, but at chlorine concentrations of less than 2-3% the pressure increase is less rapid than the intensity increase. For 436 nm. wavelength light with chlorine concentrations between 40 and 65% no dependence due to chlorine concentration was observed. For 420 nm. wavelength light with chlorine concentrations between 4 and 57% there was also no dependence on chlorine concentration. However, for 365 nm. wavelength light, there was variation due to chlorine concentration. At this wavelength there was no variation at chlorine concentrations above 2.5-3%; but at chlorine concentrations below 2.5-3% the rate increased with decreasing chlorine concentration. The effect of wavelength on the rate of pressure increase was such that the lower wavelength gave a greater rate at the same intensity. At the temperature range of 20 to 30°C.

there was no dependence on temperature within the experimental error over the wavelength range covered. The quantum yields for destruction of O_3 were $\phi_{313}:\phi_{365}:\phi_{420}:\phi_{436} = 1:0.84:0.77:0.67$, where $\phi_{365} = 2.6$. When the study was continued using high ozone concentrations (8-68%) but low chlorine concentrations (less than 4%) some interesting results were encountered. The relationship between absorbed light intensity and rate approached an $I_{abs}^{0.5}$ relationship. The quantum yield increased from a level of 2-3, to a maximum of 59 indicating a chain mechanism. The system also became dependent on temperature. Allmand and Spinks also found indirect evidence for the presence of chlorine trioxide as an intermediate. They presented the following mechanism to explain their data and that of earlier workers.

$$Cl_2 + h\nu \longrightarrow 2\ Cl \qquad (17)$$

$$Cl + O_3 + M \longrightarrow ClO_3^* + M \qquad (20)$$

$$ClO_3^* \longrightarrow ClO_3 \qquad (21)$$

$$ClO_3 \longrightarrow \underline{ClO_3} \qquad (22)$$

$$2\ \underline{ClO_3} \longrightarrow Cl_2 + 3\ O_2 \qquad (23)$$

$$2\ \underline{ClO_3} \longrightarrow \underline{Cl_2O_6} \qquad (24)$$

$$\underline{Cl_2O_6} \longrightarrow Cl_2 + 3\ O_2 \qquad (25)$$

(A)		(B)	
$ClO_3^* + O_3 \longrightarrow ClO_2 + 2\ O_2$	(26)	$\underline{ClO_3} + O_3 \longrightarrow ClO_2 + 2\ O_2$	(27)
$ClO_2 + O_3 \longrightarrow ClO_3 + O_2$	(10)	$ClO_2 + O_3 \longrightarrow ClO_3 + O_2$.	(10)

The ClO_3^* is represented as containing excess energy while the underlined species are absorbed on the wall of the reactor. The symbol $\underline{M}$ represents any available third body. The first seven reactions represent what occurs when there is no chain formation while parts (A) and (B) represent two distinct chain mechanisms. Allmand and Spinks did not use the formation of chlorine

dioxide as a key step in the mechanism because they could find no evidence of its presence through its characteristic spectrum. Again a number of the equations of this mechanism seem erroneous in light of recent understanding. Equations (20), (23), and (25) all require excessive atomic rearrangement and similar reactions have already been rejected. Equation (21) could easily occur if a second body was present to carry off energy. Equations (22) and (24) could easily be the means through which chlorine trioxide dimerizes to dichlorine hexoxide. Since Equation (11) has been accepted, Equations (26) and (27) can be considered probable.

Heidt, et al. (39) also monitored the system with pressure measurements. They used light of wavelength 366 nm., chlorine pressures of 60-490 mm. Hg, and ozone pressures of 55-590 mm. Hg at temperatures of 2, 13, and 22°C. in quartz and 23, 35, and 50°C. in pyrex. Their results were quite erratic despite precautions taken to purify gases and eliminate sources of impurities. Heidt, et al. (39) declined to make any meaningful explanation. Norrish and Neville (40), based on work that they were doing in the system, blamed the problems of Heidt, et al. on the condensation of chlorine trioxide to dichlorine hexoxide at the walls of the reaction vessel. Norrish and Neville found that this condensation occurred at chlorine and ozone pressures above 100 mm. Hg. Norrish and Neville also showed that the rate of decomposition of dichlorine hexoxide was of the order of the dark reaction of Heidt, et al. (they encountered a continued increase in pressure after stopping illumination). Furthermore, with the condensation of dichlorine hexoxide the use of pressure measurements for determination of the rate of decomposition of ozone and for calculation of quantum yield is erroneous. Norrish and Neville report that at pressures of chlorine and ozone where dichlorine hexoxide does not condense the data become quite reproducible.

Byrns (41) and Byrns and Rollefson (42,43,44) report further work on the system. They have given positive evidence for the formation of dichlorine hexoxide and dichlorine heptoxide (Cl_2O_7) at temperatures of 0, 20, and 30°C. Dichlorine hexoxide was assumed to be present because of the observation of its characteristic red color. Dichlorine heptoxide was shown to be present by measurement of the vapor pressure of a colorless oil found after repeated reactions and comparison of this vapor pressure curve with that obtained by Goodeve and Powney (45) for dichlorine heptoxide. Byrns and Rollefson recognized from this that pressure changes could not be used to fully understand the system and that quantitative elucidation of the system is dependent on chlorine trioxide and dichlorine heptoxide. They did make some studies of the system using blue light to illuminate mixtures containing chlorine at pressures of 10-50 cm. H_2SO_4 and ozone at pressures of 30-82 cm. H_2SO_4 with a total pressure of 0.25 atm. The formation of dichlorine heptoxide is proportional to the initial ozone pressure, increases slightly with increase in chlorine concentration and absorbed light intensity, and shows a slight dependency on temperature between 20 and 30°C. Further observations on the entire system include a change in pressure which is dependent on initial ozone pressure, and is independent of absorbed light intensity and chlorine pressure. They feel that there is an induction period during which concentrations of intermediates build up. They did not present a mechanism for the entire system but suggest that the initial formation of chlorine trioxide is through Equation (18) or (28),

$$Cl + O_3 \longrightarrow ClO_3 \qquad (18)$$

$$Cl + O_3 + M \longrightarrow ClO_3 + M. \qquad (28)$$

Equation (18) has been discussed previously and Equation (28) is essentially Equation (20). None of these equations appears applicable because of the need for excessive atomic rearrangement. Byrns and Rollefson also studied three reactions involving chlorine trioxide which they felt must be accounted for in any reaction mechanism for the system. The first of these is a reaction between ozone and chlorine trioxide which decomposes ozone in a chain mechanism but also forms dichlorine heptoxide. These reactions were run at 0 and 20°C. and were followed by pressure measurements. Dichlorine hexoxide was added to a vessel, the ozone was added and the pressure increase followed. At first they thought that no chlorine trioxide was decomposed, but when ozone was continually added to the system eventually they obtained positive evidence for dichlorine heptoxide through vapor pressure data. They also deduced through the increase in pressure data that the decomposition of ozone was a chain mechanism which was inhibited to the same extent by the third bodies oxygen, nitrogen (N_2), and chlorine. They felt that wall reactions were not important. The following mechanism was presented to account for the reaction between chlorine trioxide and ozone.

$$ClO_3 + O_3 \longrightarrow ClO_2 + 2\ O_2 \qquad (11)$$

$$ClO_2 + O_3 \longrightarrow ClO_3^* + O_2 \qquad (29)$$

$$ClO_3^* + O_3 \longrightarrow ClO_2 + 2\ O_2 \qquad (26)$$

$$ClO_3^* + M \longrightarrow ClO_3 + M + k.e. \qquad (30)$$

$$ClO_3^* + O_3 \longrightarrow ClO_4 + O_2 \qquad (31)$$

$$ClO_3 + ClO_4 \longrightarrow Cl_2O_7. \qquad (32)$$

Byrns and Rollefson envisioned ClO_3^* as an activated or peroxide structure of chlorine trioxide. Equation (11) initiates the chain while Equations (29) and (26) propagate the chain. Equations (30), (31), and (32) are chain

termination steps. All of these reactions seem quite feasible. However, because of the atomic rearrangement required it seems difficult for Equation (31) to occur if ClO_3* is considered to have a peroxide structure. An activated chlorine trioxide seems more acceptable. In light of the discussion that follows on the thermal decomposition of chlorine trioxide, Equation (11) could be replaced by Equation (33),

$$2\ ClO_3 \longrightarrow 2\ ClO_2 + O_2, \qquad (33)$$

and the rest of the mechanism could remain intact. Byrns and Rollefson also studied the thermal decomposition of chlorine trioxide. This was done by forming and purifying dichlorine hexoxide in a reactor and then monitoring the pressure increase at temperatures of 0 and 30°C. Other work used smaller amounts of dichlorine hexoxide so that the decomposition could go to completion. The products were determined by pressure difference methods, where all of the gases except oxygen were condensed out by liquid air. This method showed that at 0°C. all of the chlorine trioxide decomposed to chlorine dioxide and oxygen by Equation (33), while at 30°C. 50% of the chlorine trioxide decomposed to chlorine dioxide and oxygen and 50% decomposed to chlorine and oxygen. Byrns and Rollefson feel that the formation of chlorine and oxygen is not by Equation (12),

$$ClO_3 + ClO_3 \longrightarrow Cl_2 + 3\ O_2. \qquad (12)$$

The most likely route of decomposition of chlorine trioxide would be through Equation (33) with subsequent decomposition of chlorine dioxide to oxygen and chlorine in a complex manner as will be shown later. Some authors (46) feel that the thermal decomposition of chlorine trioxide proceeds by Equation (34),

$$2\ ClO_3 \longrightarrow ClO_2 + ClO_4. \qquad (34)$$

However, this will be discussed in a later section and discarded as a possibility. Byrns and Rollefson also studied a chlorine-sensitized decomposition of chlorine trioxide. They found that the blue light used in the study did not decompose chlorine trioxide but when chlorine was added and the system illuminated by the blue light the subsequent formation of chlorine atom caused the chlorine trioxide to decompose. This work was done by having the chlorine trioxide in equilibrium with dichlorine hexoxide and measuring a pressure increase. They gave a short mechanism which they considered quite uncertain.

$$Cl_2 + h\nu \longrightarrow 2\ Cl \qquad (17)$$

$$Cl + ClO_3 \longrightarrow Cl_2O_3 \qquad (35)$$

$$Cl + Cl_2O_3 \longrightarrow Cl_2 + Cl + 3/2\ O_2. \qquad (36)$$

They felt that Equation (17) was the only certain one while Equation (35) accounted for a decrease in pressure that they encountered. They admit that Equation (36) is improbable but offered it in lieu of a better explanation. This phenomenon of a chlorine-sensitized decomposition might be real or it may be the thermal decomposition of chlorine trioxide by Equation (33) followed by Equation (37),

$$ClO_2 + Cl \longrightarrow 2\ ClO, \qquad (37)$$

then subsequent breakdown of ClO. Equation (37) is known to occur and has been used by a number of investigators (47,48) to obtain a pure stream of ClO for studies of its decomposition. Using a similar equation, the direct reaction between chlorine atom and chlorine trioxide may be as shown in Equation (38),

$$ClO_3 + Cl \longrightarrow ClO_2 + ClO, \qquad (38)$$

with subsequent decomposition of chlorine dioxide as in Equation (37) and breakdown of ClO. Photochemical decomposition of chlorine dioxide can be ruled out since Byrns and Rollefson reported no reaction when only chlorine trioxide was illuminated with this wavelength light.

Norrish and Neville (49) in 1934 did the most recent study of the photochemical system. They used a quartz reactor kept at a constant temperature of 25°C. The reaction was followed by pressure measurements and light of wavelength 365 nm. was used to activate the reaction. Care was taken to make their experimental runs under conditions where chlorine trioxide did not condense out. Their results were similar to those reported by previous authors. Under conditions of high ozone and low chlorine and oxygen pressures, the quantum yield of ozone decomposition is proportional to $I_{abs}^{-0.5}$ and approaches ten indicating a chain mechanism. When the pressures of chlorine and oxygen are high, the quantum yield of ozone decomposition decreases to a limiting value of two and is independent of absorbed light. The rate of decomposition of ozone is zero order with respect to ozone. The introduction of nitrogen and carbon dioxide (CO_2) had no effect on the system. Norrish and Neville presented the following mechanism, based on ClO as the chain carrier for the decomposition of ozone.

$$Cl_2 + h\nu \longrightarrow 2\ Cl \qquad (17)$$

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (39)$$

$$ClO + O_3 \longrightarrow Cl + 2\ O_2 \qquad (40)$$

$$ClO + ClO \longrightarrow Cl_2 + O_2 \qquad (14)$$

$$Cl + O_3 + Cl_2 \longrightarrow ClO_3 + Cl_2 \qquad (41)$$

$$Cl + O_3 + O_2 \longrightarrow ClO_3 + O_2. \qquad (42)$$

Equations (41) and (42) are further explained by the following:

$$Cl + Cl_2 \longrightarrow Cl_3 \tag{43}$$

$$Cl_3 + O_3 \longrightarrow ClO_3 + Cl_2 \tag{44}$$

$$Cl + O_2 \longrightarrow ClO_2 \tag{19}$$

$$ClO_2 + O_3 \longrightarrow ClO_3 + O_2. \tag{10}$$

In this mechanism Equation (17) initiates the chain. Equations (39) and (40) propagate the chains. Equation (14) terminates the chain leading to the $I_{abs}^{-0.5}$ relationship while Equations (41) and (42) terminate the chains by inhibition of chlorine and oxygen, leading to a quantum yield independent of I_{abs}, a rate equation zero order with respect to ozone, and formation of dichlorine hexoxide. Norrish and Neville give several arguments why chlorine trioxide cannot be a chain carrier. First, since chlorine trioxide is assumed to reach its greatest concentration under conditions of high chlorine concentration, where it condenses out, one would expect the ozone to be decomposed at its fastest rate under these conditions if chlorine trioxide were the carrier; however, under these conditions the quantum yield of ozone decomposition reaches a limiting value. The second argument involves the termination of chains. If chlorine trioxide is the chain carrier then the termination of chains by chlorine trioxide would be expected to cause an $I_{abs}^{-0.5}$ relationship with the quantum yield which was not observed in systems of high chlorine and oxygen concentrations. Norrish and Neville feel that the inhibiting effect of chlorine and oxygen must be accounted for by the termination of chains and the formation of chlorine trioxide as indicated by Equations (41) and (42) and not because of simple ternary collisions because they found no effect due to nitrogen and carbon dioxide. By manipulation of the given mechanism, Norrish and Neville obtained the following rate, and quantum yield expressions.

For low oxygen, low chlorine, and high ozone concentrations, when Equation (14) predominates as the chain-ending mechanism, these expressions become:

$$\frac{-d\,[O_3]}{dt} = 2\,I_{abs} + 2\sqrt{2/k_{14}} \cdot k_{40}\,[O_3]\sqrt{I_{abs}}, \text{ and} \tag{45}$$

$$\phi = 2 + 2\sqrt{2/k_{14}} \cdot k_{40}\,[O_3]/\sqrt{I_{abs}}. \tag{46}$$

For high oxygen or chlorine and low ozone concentrations, when Equations (41) and (42) predominate as the chain-ending mechanism, these expressions become:

$$\frac{-d\,[O_3]}{dt} = 2\,I_{abs} + 4\,k_{39}I_{abs}/(k_{42}[O_2] + k_{41}\,[Cl_2]), \text{ and} \tag{47}$$

$$\phi = 2 + 4\,k_{39}/(k_{42}[O_2] + k_{41}\,[Cl_2]). \tag{48}$$

Norrish and Neville feel that these expressions comply with all of the known data about the system. They then extended their mechanism to account for the thermal reaction between ozone and chlorine. They gave the following as this mechanism and expressed its virtue as being able to explain both systems with essentially the same mechanism.

$$Cl_2 + O_3 \longrightarrow ClO + ClO_2 \tag{15}$$

$$ClO + O_3 \longrightarrow Cl + 2\,O_2 \tag{40}$$

$$Cl + O_3 \longrightarrow ClO + O_2 \tag{39}$$

$$ClO + ClO \longrightarrow Cl_2 + O_2 \tag{14}$$

$$ClO_2 + O_3 \longrightarrow ClO_3 + O_2. \tag{10}$$

Manipulation of the reactions of this mechanism also resulted in a rate expression similar to that given by Bodenstein, et al. (33) for the thermal reaction.

$$\frac{-d\,[O_3]}{dt} = \text{const.} \times [Cl_2]^{1/2}\,[O_3]^{3/2} \qquad (49)$$

Although the basic experimental evidence of Norrish and Neville is probably valid, the suggested mechanism seems somewhat in doubt. Equations (17), (39), and (40) of their mechanism seem quite valid. However, Equation (14) as already mentioned is no longer the accepted manner in which ClO decomposes to chlorine and oxygen. Equations (41) and (42) seem highly erroneous. Equation (41) is explained by the two-step mechanism of Equations (43) and (44). Although Equation (43) is quite valid, being the first step in the recombination of chlorine atoms due to the chlorine molecule (25), Equation (44) seems improbable because of the excessive atomic rearrangements that would be required. Equation (42) is explained by Equations (19) and (10). It has already been noted that the product of Equation (19) is ClOO if a third body is present. It appears that for ClOO to react with ozone there would again be problems because of excessive atomic rearrangement. In the suggested mechanism for thermal decomposition of ozone in chlorine, Equations (14) and (15) have already been questioned. Equations (39) and (40) are acceptable. Equation (10) is acceptable if the ClO_2 species is chlorine dioxide and not the peroxide (ClOO).

Although they did not do any experimental work on the system, Goodeve and Marsh (50) discussed it in light of stepwise reactions leading to the formation of dichlorine heptoxide. Their basic mechanism for the formation of dichlorine heptoxide contains four reactions,

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (39)$$

$$ClO + O_3 \longrightarrow ClO_2 + O_2. \qquad (50)$$

$$ClO_2 + O_3 \longrightarrow ClO_3 + O_2 \quad (10)$$

$$2\ ClO_3 + O_3 \longrightarrow Cl_2O_7 + O_2. \quad (51)$$

Since chlorine dioxide and chlorine trioxide are formed with evolution of excess heat, they feel that thermal reactions of these species could occur.

$$ClO_2 \longrightarrow Cl + O_2 \quad (52)$$

$$ClO_3 \longrightarrow ClO + O_2. \quad (53)$$

The following reactions were then suggested as occurring to help account for the high quantum yield of ozone decomposition.

$$ClO + O_3 \longrightarrow Cl + 2\ O_2 \quad (40)$$

$$ClO_2 + O_3 \longrightarrow ClO + 2\ O_2 \quad (54)$$

$$ClO_3 + O_3 \longrightarrow ClO_2 + 2\ O_2. \quad (11)$$

Goodeve and Marsh considered the thermal reaction between chlorine and ozone in a similar manner. Previous authors in this study have suggested that Equation (15),

$$Cl_2 + O_3 \longrightarrow ClO + ClO_2, \quad (15)$$

is the initiating reaction and this along with the above reactions could account for the thermal reaction. Goodeve and Marsh have suggested that the initial reaction is the thermal breakdown of ozone to an oxygen molecule and oxygen atom and the subsequent reaction of oxygen atoms with chlorine to form ClO and chlorine atoms.

$$O_3 \longrightarrow O_2 + O \quad (55)$$

$$Cl_2 + O \longrightarrow ClO + Cl. \quad (56)$$

The formation of chlorine atoms and ClO would then start the chain sequence. These ideas of Goodeve and Marsh appear quite valid. Equations (39), (50), (10), (51), (40), (54), and (11) are easily acceptable. However, Equation (52) seems doubtful because of the atomic rearrangement needed. Equation (53) does not appear feasible in light of the work of Byrns and Rollefson (44). Equation (55) should probably be written in the more accepted form using a neutral body to carry off energy as suggested by Axworthy and Benson (31).

$$O_3 + M \longrightarrow O_2 + O + M. \qquad (57)$$

Equation (56) is acceptable and has been studied recently by Niki and Weinstock (51).

Papers by Szabo (52,53) and Huhn, et al. (54) discuss the importance of ClO and chlorine trioxide as chain carriers in both the thermal and photochemical reactions of chlorine and ozone as well as the thermal and photochemical decomposition of dichlorine monoxide and chlorine dioxide. They suggest that all of these reactions are fundamentally the same and that the key is an equilibrium relationship set up between ClO and chlorine trioxide, where chlorine trioxide predominates at low temperatures and ClO predominates at the higher temperatures. This equilibrium relationship is

$$ClO + O_2 \rightleftharpoons ClO_3 \rightleftharpoons 1/2\ Cl_2O_6. \qquad (58)$$

They suggest that ClO is the actual chain carrier and that the presence of chlorine trioxide is merely a result of the concentration of ClO and the temperature of the system. Using this equilibrium they suggest that all mechanisms which use chlorine trioxide as the chain carrier can be changed so that ClO is the chain carrier and still account for the presence of chlorine trioxide in the system. This argument sounds good but McHale and von Elbe (23) have noted

that the value of $H^{\circ}_{f_{298}}$ - 37 kcal./mole for ClO used by Szabo is erroneous and has been shown to be 24.2 kcal./mole (55). This new value means that there is no possibility for this type of equilibrium. Furthermore, extensive work in chlorine-oxygen photolysis has never found chlorine trioxide as a product.

Schumacher (56) in 1957 considered the thermal reaction and accounted for the formation of dichlorine heptoxide. The chain carrier is considered to be chlorine trioxide. The mechanism is given as:

$$Cl_2 + O_3 \longrightarrow ClO + ClO_2 \qquad (15)$$

$$ClO_2 + O_3 \longrightarrow ClO_3 + O_2 \qquad (10)$$

$$ClO_3 + O_3 \longrightarrow ClO_2 + 2\ O_2 \qquad (11)$$

$$2\ ClO_3 \longrightarrow 2\ ClO_2 + O_2 \qquad (33)$$

$$2\ ClO_3 \longrightarrow ClO_2 + ClO_4 \qquad (34)$$

$$ClO_3 + ClO_4 \longrightarrow Cl_2O_7 \qquad (32)$$

$$ClO_3 + ClO_3 \longrightarrow Cl_2 + 3\ O_2 \qquad (12)$$

$$ClO + ClO \longrightarrow Cl_2 + O_2. \qquad (14)$$

This mechanism appears to be the final conclusion of Schumacher who has worked in this area since 1929. The mechanism still has in it Equation (15) which does not appear possible due to the atomic rearrangements necessary. Equations (12) and (14) still appear although literature indicates that they do not occur in this manner. Equations (10), (11), (33), (34), and (32) all are acceptable, although a later discussion will question the validity of Equation (34).

Edgecombe, et al. (57) have considered the photochemical and thermal reactions of chlorine and ozone in light of recent work done in flash photolysis. They feel that ClO is the chain carrier in the reaction based on its reactivity shown in flash photolysis work.

McGrath and Norrish (58) report flash photolysis of mixtures of chlorine and ozone with excess inert gas. Under conditions where only chlorine is dissociated they propose a reaction scheme which is the same as that proposed by Norrish and Neville (49) for the steady-state reactions in the photolysis of ozone sensitized by chlorine.

$$Cl_2 + h\nu \longrightarrow Cl(^2P_{3/2}) + Cl(^2P_{1/2}) \qquad (17)$$

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (39)$$

$$ClO + O_3 \longrightarrow Cl + 2\,O_2. \qquad (40)$$

McGrath and Norrish found that under certain concentration conditions chlorine trioxide was also formed.

The author would like to point out an apparent error in the review of Schmeisser and Brandle (5) in which they state that no chlorine trioxide is formed when light which is absorbed by chlorine is used to activate the ozone-chlorine system. There is overwhelming evidence for this occurrence. It appears that Schmeisser and Brandle did not do a thorough review since they only referred to Bodenstein, et al. (12) and Bodenstein and Schumacher (32).

PHOTOCHEMICAL CHLORINE-OZONE SYSTEM, ESTABLISHED FACTS

The following conclusions have been drawn up as a sum total of all those workers in the area. To find out which can be attributed to which author, refer to the preceding section. These conclusions are based on measurements of pressure difference and, as the preceding section indicates, pressure measurements are somewhat in error because of formation and condensation of dichlorine hexoxide and dichlorine heptoxide. These conclusions are also based in most cases on the decomposition of ozone.

IN GENERAL

The decomposition of ozone and subsequent formation of dichlorine hexoxide can be initiated by light absorbed by ozone or chlorine. Dichlorine hexoxide condensation is more abundant at lower temperatures. Dichlorine heptoxide has been shown to form. The lower the wavelength the faster the rate of decomposition of ozone and the larger the quantum yield. A short induction period is reported. The decomposition of ozone occurs in a chain mechanism. Also, before complete decomposition of ozone occurs, there is a rapid increase in the rate of decomposition.

HIGH OZONE, LOW CHLORINE AND OXYGEN PRESSURES

Under these conditions the rate of decomposition of ozone is dependent on the absorbed light intensity in a half power relationship, $I_{abs}^{0.5}$. The quantum yield has been recorded as high as 59 and follows a $I_{abs}^{-0.5}$ relationship. The mechanism of ozone decomposition is definitely a chain mechanism. There is a dependence on temperature.

HIGH OR LOW OZONE, HIGH CHLORINE AND OXYGEN PRESSURES

These conditions produce a relationship for ozone decomposition zero order with respect to ozone and proportional to absorbed light intensity. The quantum yield is independent of absorbed light intensity and reaches a limiting value of 2. Therefore, the chain mechanism for the destruction of ozone must be inhibited. No effect due to introduction of nitrogen and carbon dioxide has been reported. As higher pressures (above 100 mm. Hg) of ozone and chlorine are used, condensation of chlorine trioxide to dichlorine hexoxide becomes evident.

FORMATION OF DICHLORINE HEPTOXIDE

The formation of dichlorine heptoxide was found to be increased by increasing the initial pressure of ozone. Its formation also increases slightly due to increases of chlorine concentration and light intensity.

REACTIONS OF CHLORINE DIOXIDE AND CHLORINE TRIOXIDE RELATED TO THE CHLORINE-OZONE SYSTEM

Szabo (52) has suggested that the reaction mechanisms of thermal and photochemical decomposition of chlorine dioxide and dichlorine monoxide are very similar and compare with those of the thermal and photochemical decomposition of ozone in chlorine, since many of the same intermediates and products are found.

PHOTOCHEMICAL DECOMPOSITION OF CHLORINE DIOXIDE

Bowen (59) was the first to show that dichlorine hexoxide was a product of the decomposition of chlorine dioxide by light, 460 nm. Bodenstein, et al. (12) also noted this and used the method to produce dichlorine hexoxide for studies of physical and chemical properties. Booth and Bowen (60) found that upon exposure to sunlight the dichlorine hexoxide formed from chlorine dioxide is converted to dichlorine heptoxide with about 60% of the original chlorine dioxide being converted to dichlorine heptoxide. Spinks (61) and Spinks and Porter (62) have also studied the photochemical decomposition of chlorine dioxide. They used light of wavelength 365 nm. They found much more abundant formation of dichlorine hexoxide at 17°C. than at 31°C. The decomposition of chlorine dioxide appears to occur in a chain mechanism since the quantum yield of destruction of chlorine dioxide was reported as 12. There was also indirect evidence for the formation of dichlorine heptoxide; heating

of the reactor was required to get a theoretical pressure rise. The authors present the following partial mechanism for photochemical decomposition of chlorine dioxide.

$$ClO_2 + h\nu \longrightarrow ClO + O \quad (59)$$

$$ClO_2 + O + M \longrightarrow ClO_3 + M \quad (60)$$

$$2\ ClO_3 \longrightarrow Cl_2O_6 \quad (13)$$

$$ClO + ClO \longrightarrow Cl_2 + O_2 \quad (14)$$

$$ClO_3 + ClO_3 \longrightarrow Cl_2 + 3\ O_2. \quad (12)$$

The authors feel that Equation (13) predominates at the lower temperatures while Equation (12) predominates at higher temperatures. This mechanism is incomplete because it does not account for the chain destruction of chlorine dioxide and production of dichlorine heptoxide. As discussed previously, Equations (12) and (14) are questionable. However, Equations (13), (59), and (60) seem quite acceptable. Equation (59) is the acceptable manner in which chlorine dioxide breaks down upon absorption of light of wavelength 365 nm. Equation (60) appears logical with no excessive atomic rearrangement needed.

Spinks and Taube (63,64) did a study of the photodecomposition of chlorine dioxide in carbon tetrachloride using 365 and 436 nm. wavelength light. They felt that their results showed that the mechanism of decomposition in carbon tetrachloride was similar to that in the vapor state. They had evidence for the formation of dichlorine hexoxide and dichlorine heptoxide through the analysis of the ionic chlorine species formed when the carbon tetrachloride was extracted by water. The occurrence of these species was less as the temperature increased, and also depended on initial concentration, light intensity, and time of illumination. After complete decomposition, only chlorine, oxygen, and dichlorine heptoxide were left in the system. A mechanism was given to explain the system.

$$ClO_2 + h\nu \longrightarrow ClO + O \quad (59)$$

$$ClO_2 + O + M \longrightarrow ClO_3 + M \quad (60)$$

$$ClO + ClO_2 \longrightarrow Cl_2O + O_2 \quad (61)$$

$$ClO + ClO \longrightarrow Cl_2 + O_2 \quad (14)$$

$$O + O + M \longrightarrow O_2 + M \quad (62)$$

$$2\ ClO_3 \longrightarrow Cl_2O_6 \quad (13)$$

$$Cl_2O_6 + O \longrightarrow Cl_2O_7. \quad (63)$$

This mechanism appears very acceptable except for Equation (14) which has been discussed before and Equation (61) which appears to require excessive atomic rearrangement.

In studies of the flash photolysis of chlorine dioxide, Lipscombe, et al. (65) found evidence for the formation of chlorine trioxide. The formation of chlorine trioxide in these studies was independent of the inert gas nitrogen or carbon dioxide and was greater at lower flash energies. They gave the following reaction for the formation of chlorine trioxide:

$$ClO_2 + O \longrightarrow ClO_3. \quad (64)$$

They ruled out the following reactions as causing the formation of chlorine trioxide:

$$ClO_2 + O + M \longrightarrow ClO_3 + M \quad (60)$$

$$ClO + O_2 \longrightarrow ClO_3 \quad (65)$$

$$ClO + O_2^* \longrightarrow ClO_3. \quad (66)$$

Equation (60) was ruled out because of the absence of an inert gas effect. Equation (65) was ruled out because of thermodynamic considerations. Equation (66) was ruled out because experimental evidence showed that the same amount of chlorine trioxide was found even if the amount of vibrationally excited oxygen (O_2*) in the system was rapidly removed. Under conditions of higher flash energies they suggest that the following reaction occurs to remove chlorine trioxide:

$$ClO_3 + h\nu \longrightarrow ClO + O_2^*. \qquad (67)$$

The conclusion of Lipscombe, et al. seems quite valid. However, the throwing out of Equation (60) and replacement with Equation (64) because of lack of an inert gas effect may be erroneous, since the nitrogen and carbon dioxide used may be very inefficient energy carriers in this system. Equation (67) also seems somewhat in doubt because of the atomic rearrangement involved.

THERMAL REACTIONS OF CHLORINE DIOXIDE

The thermal decomposition of chlorine dioxide also has been studied extensively. It appears that McHale and von Elbe (23), and Crawford and DeWitt (66) have done the latest studies in this area. Since McHale and von Elbe's study was done in the absence of water, this paper will be stressed. McHale and von Elbe studied the thermal decomposition of chlorine dioxide by observing the induction time needed for the explosion of chlorine dioxide at temperatures ranging from 54 to 134°C. They found that added inert gases, oxygen, chlorine, helium (He), and nitrogen, all had the same effect of shortening the induction time. The more inert the gas the shorter the induction time. They attributed this to the slowing of diffusion rates of radicals to the wall where chain termination would occur and not to bi- and termolecular collisions.

The induction time decreases with increasing temperature. It was shown that the presence of dichlorine heptoxide had no effect while the presence of chlorine trioxide increased the induction time. Previous irradiation of the chlorine dioxide shortened the induction time. Dichlorine trioxide (Cl_2O_3) was isolated and its introduction to the chlorine dioxide system and the subsequent shortening of the induction time lead McHale and von Elbe to the following interpretation. Dichlorine trioxide was the intermediate necessary to explain the degenerate chain-branching explosion of chlorine dioxide. However, the manner in which McHale and von Elbe isolated dichlorine trioxide leads one to believe that they could have easily had a mixture of ClO and ClOO. They made no attempt to determine if ClO might be the chain carrier. The mechanism for the thermal decomposition of chlorine dioxide is given by McHale and von Elbe as:

$$2\ ClO_2 \xrightarrow{\text{wall}} ClO + ClO_3 \qquad (68)$$

$$ClO + ClO_2 \longrightarrow Cl_2O_3 \qquad (69)$$

$$ClO + Cl_2O_3 \longrightarrow ClO_2 + ClOOCl \qquad (70)$$

$$ClOOCl \longrightarrow ClOO + Cl \qquad (71)$$

$$ClOO \longrightarrow Cl + O_2 \qquad (72)$$

$$ClO_2 + Cl \longrightarrow 2\ ClO \qquad (37)$$

$$ClO_2 + Cl \longrightarrow Cl_2 + O_2 \qquad (73)$$

$$Cl \xrightarrow{\text{wall}} 1/2\ Cl_2. \qquad (74)$$

This mechanism is unique in that it uses some of the chlorine oxides formed during photolysis of chlorine in the presence of oxygen. Equations (69), (70), (71), and (72) could easily be replaced by much of the mechanism suggested by Johnston, et al. (35) which will be presented shortly. Equations (69) and (70)

are somewhat doubtful as indicated by the discussion of dichlorine trioxide presented above. Equation (68) seems reasonable as do Equations (37) and (74). However, Equation (73) seems inappropriate because of required atomic rearrangements and because Equation (37) is probably the first step in the total breakdown of chlorine dioxide to chlorine and oxygen.

Individual reactions of chlorine dioxide with chlorine atoms, oxygen atoms, and ozone have already been implied. Ones that appear acceptable are as follows:

$$ClO_2 + Cl \longrightarrow 2\ ClO \qquad (37)$$

$$ClO_2 + O \longrightarrow ClO + O_2 \qquad (75)$$

$$ClO_2 + O + M \longrightarrow ClO_3 + M \qquad (60)$$

$$ClO_2 + O_3 \longrightarrow ClO_3 + O_2. \qquad (10)$$

Equations (37), (60), and (10) have already been discussed. Equation (60) is preferred over Equation (64) because there is a provision for carrying away of energy. Equation (75) which was studied by Clyne and Coxon (67) probably represents much better than Equation (64) what happens when chlorine dioxide and oxygen atoms collide in the absence of a third body.

REACTIONS OF CHLORINE TRIOXIDE

Reactions of chlorine trioxide which may occur in the chlorine-ozone system have been suggested in a number of works. The photochemical decomposition of chlorine trioxide by 365 nm. wavelength light has been established by Kalina and Spinks (68) and Goodeve and Richardson (69). Although these authors do not give a reaction to account for this it is assumed on the basis of the equation given for chlorine dioxide photodecomposition that the following reaction could account for this occurrence:

$$ClO_3 + h\nu \longrightarrow ClO_2 + O. \qquad (76)$$

Equation (76) seems to be more explainable than Equation (67),

$$ClO_3 + h\nu \longrightarrow ClO + O_2^*. \qquad (67)$$

The thermal decomposition of chlorine trioxide has been discussed by Byrns (41) and Byrns and Rollefson (44). Equation (33),

$$2\ ClO_3 \longrightarrow 2\ ClO_2 + O_2, \qquad (33)$$

accounts for the formation of chlorine dioxide. The more abundant formation of chlorine and oxygen at temperatures above 30°C. is probably due to thermal degradation of chlorine dioxide. A chlorine sensitized decomposition of chlorine trioxide was also shown by Byrns (41), Byrns and Rollefson (44), and Kalina and Spinks (68). Earlier remarks suggested Equation (38) as the means of this breakdown.

$$ClO_3 + Cl \longrightarrow ClO_2 + ClO. \qquad (38)$$

Further decomposition of ClO and chlorine dioxide would then occur. It has also been shown by Rollefson and Byrns (42) and Goodeve and Richardson (70) that small amounts of dichlorine heptoxide are formed when chlorine trioxide is formed from chlorine dioxide and ozone. Dichlorine heptoxide has also been shown to form in the photolysis of chlorine dioxide (60-64) and the thermal (56) and photochemical destruction of ozone in chlorine (44). Equations presented to explain this formation are:

$$2\ ClO_3 + O_3 \longrightarrow Cl_2O_7 + O_2 \qquad (51)$$

$$Cl_2O_6 + O \longrightarrow Cl_2O_7 \qquad (63)$$

$$2\ ClO_3 \longrightarrow ClO_2 + ClO_4 \qquad (34)$$

$$ClO_3 + ClO_4 \longrightarrow Cl_2O_7. \qquad (32)$$

Arvia, et al. (46) made an interesting study of the thermal decomposition of dichlorine hexoxide in the presence of fluorine at a pressure range of 40-375 mm. Hg and temperatures of 22-48°C. The products consisted of 70-75% chloryl fluoride ($FClO_2$), about 25% dichlorine heptoxide, and a little chlorine, fluorine perchlorate ($FClO_4$), and oxygen. They suggested that fluorine did not react directly with dichlorine hexoxide but with its thermal decomposition products. This accounted for chloryl fluoride. The dichlorine heptoxide was from the chlorine tetroxide (ClO_4) and chlorine trioxide in the system, while the fluorine perchlorate was from the small amount of chlorine tetroxide that did not react to form dichlorine heptoxide. The presence of chlorine tetroxide was accounted for by the thermal decomposition of chlorine trioxide to chlorine dioxide and chlorine tetroxide,

$$2\ ClO_3 \longrightarrow ClO_2 + ClO_4. \qquad (34)$$

The formation of dichlorine heptoxide in this system was used by Arvia, et al. to justify a reaction of chlorine trioxide and chlorine tetroxide to form dichlorine heptoxide in photochemical and thermal decomposition of ozone by chlorine,

$$ClO_3 + ClO_4 \longrightarrow Cl_2O_7. \qquad (32)$$

However, if Equation (34) is considered a major reaction in thermal degradation of chlorine trioxide and Equation (32) accounts for formation of dichlorine heptoxide, one should find an abundance of dichlorine heptoxide after thermal degradation of chlorine trioxide; the existing literature gives no evidence for this.

PHOTOLYSIS OF CHLORINE IN THE PRESENCE OF OXYGEN

Because oxygen is being produced during photolysis of the chlorine-ozone system it is expected that reactions occurring in the ozone-chlorine system will also include those reactions which occur during photolysis of chlorine in the presence of oxygen. Johnston, et al. (35) have published the most recent article on this system. They present the following mechanism for the photolysis of chlorine in the presence of oxygen.

$$Cl_2 + h\nu \longrightarrow Cl(^2P_{3/2}) + Cl(^2P_{1/2}) \quad (17)$$

$$Cl + O_2 + M \longrightarrow ClOO + M \quad (77)$$

$$ClOO + M \longrightarrow Cl + O_2 + M \quad (78)$$

$$Cl + ClOO \longrightarrow ClO + ClO \quad (79)$$

$$ClO + ClO \longrightarrow Cl + ClOO \quad (80)$$

$$Cl + ClOO \longrightarrow Cl_2 + O_2 \quad (81)$$

$$ClO + ClO + M \longrightarrow Cl_2O_2 + M \quad (82)$$

$$Cl_2O_2 + M \longrightarrow ClO + ClO + M \quad (83)$$

$$Cl_2O_2 + M \longrightarrow Cl_2 + O_2 + M \quad (84)$$

$$2\ Cl + M \longrightarrow Cl_2 + M. \quad (85)$$

Further work by Clyne and White (47) has shown that Equations (82), (83), and (84) occur at pressures higher than 1 atm. Equations (79), (80), and (81) as a group probably show the manner in which ClO decomposes. Equations (77)-(84) could easily be substituted into the mechanism of chlorine dioxide decomposition given by McHale and von Elbe (23). This mechanism represents the most up-to-date explanation of the photolysis of chlorine in oxygen which has been studied for the past 22 years.

PRESENTATION OF THE PROBLEM AND THESIS OBJECTIVES

The literature indicates that the chlorine-ozone photochemical system is extremely complex. The system has been studied thoroughly by a number of investigators but the last paper to appear was in 1934. These early papers based practically all of their conclusions on the monitoring of pressure rises in the system and were concerned more about the decomposition of ozone than the formation of dichlorine hexoxide and dichlorine heptoxide. The formation of dichlorine hexoxide and dichlorine heptoxide and their resultant effect on pressure measurements was recognized by later investigators but pressure measurements were still used with the reservation that a complete understanding of the system would not be possible until rates of formation of intermediates and products were known. The mechanisms for the system presented by the early investigators show that much work is still required if a complete understanding of the system is to be obtained.

Therefore, it was felt that further understanding of the chlorine-ozone photochemical system could be gained in a study with the following objectives:

1. To study the system in light of the final products formed through an analytical system which allows trapping and analysis of the expected chlorine oxides.
2. To study the effect on formation of final products caused by the variation of time, temperature, reactant concentration, light intensity, and total pressure.
3. To bring together existing literature on reactions of different chlorine oxides and the chlorine-ozone photochemical system and, in light of the present study, elucidate a possible reaction mechanism for the system.

EXPERIMENTAL

This section discusses the experimental apparatus, experimental procedure, and analytical procedures. The experimental apparatus is divided into five systems: reactor, temperature control, pressure measurement, ozonizer, and light activation. The experimental procedure is divided into three parts: initial, reaction, and recovery of products. The analytical procedures for determination of hypochlorite (ClO^-), chlorite (ClO_2^-), chlorate (ClO_3^-), perchlorate (ClO_4^-), and chloride (Cl^-) are discussed, along with their accuracy.

EXPERIMENTAL APPARATUS

REACTOR SYSTEM

Reactor

Figure 1 presents a photograph of the reactor with labeled parts. The body of the reactor was made from a Pyrex "Double-Tough" Drainline Straight Tee (Mooney Brothers Corp., Minneapolis, Minn.) with a 2.0-inch inside diameter. To it were fused two pyrex end plates made by Pope Scientific, Inc., Menominee Falls, Wis. Fitted to the third opening was a teflon manifold held by a drainline coupling. Five ports were drilled into the manifold: one for incoming streams of liquid, one for exiting streams of liquid and gas, one for insertion of a thermocouple, and one for incoming gas streams which was connected to a fifth port that goes to the pressure measurement apparatus. The ports were specially prepared to accommodate tube end fittings made by Chromatronix, Inc., Berkeley, Calif., and the bore was 0.060 in. The overall inside length of the reactor was 8.0 in. The volume was measured to be 611.6 ± 0.1 ml. Before use the reactor interior was cleaned using potassium dichromate cleaning solution, and thoroughly rinsed with distilled water.

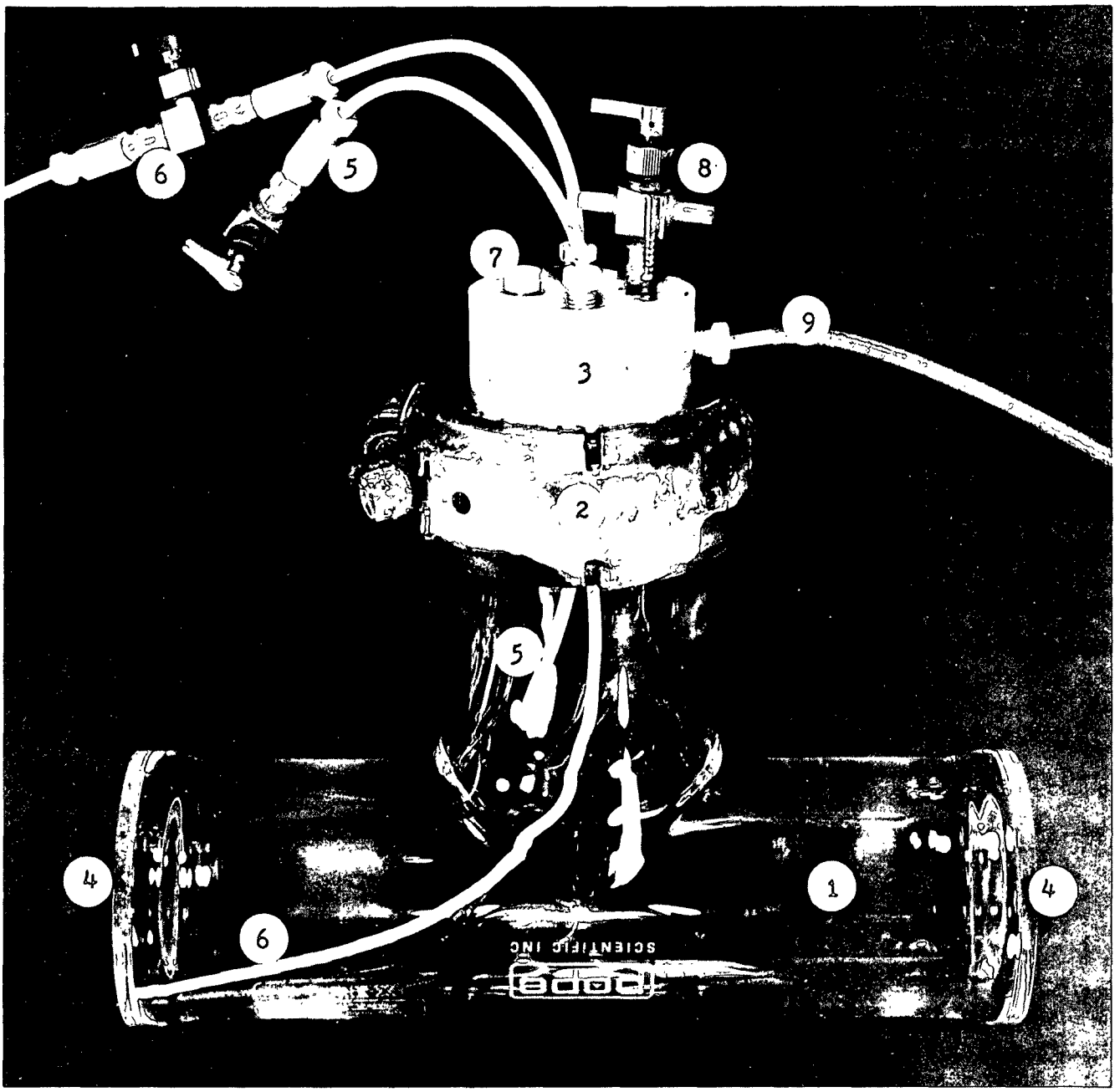


Figure 1. The Reactor

1. Reactor Body, Pyrex "Double-Tough" Drainline Straight Tee, 2"x2", Code 2211
2. Coupling, Drainline Coupling, Size 2", Code 2009
3. Teflon Manifold, Prepared at The Institute of Paper Chemistry
4. Pyrex End Plates, Fused to Reactor Body by Pope Scientific, Inc.
5. Incoming Port, for Liquids
6. Exit Port, for Liquids and Gases
7. Thermocouple Port, for Insertion of Thermocouples
8. Distribution Valve, for Entrance of Reactants
9. Pressure Measurement Line, for Pressure Measurement and Pulling Vacuum

Tubing

The tubing used in the experimental apparatus was Chromatronix, Inc. 0.063 in. I.D. and 0.125 in. O.D. teflon tubing. Also, available from Chromatronix, Inc. were various specialized fittings which allowed attachment of the tubing in various configurations. These fittings insured that only teflon or Kel-F came in contact with the liquids and gases used. Also, used with this tubing, were a Teflon Tee and Cross made at The Institute of Paper Chemistry.

Valves

The valves used were obtained from Hamilton Company, Inc., Whittier, Calif. The valves were lined with Kel-F and were supplied with male luer fittings which were attached to female luers supplied by Chromatronix, Inc., thus making the valves compatible with the Chromatronix tubing.

Gases

Gases were obtained from Matheson Gas Products, Joliet, Ill. The oxygen and chlorine were Matheson Research Grade Gases, 99.99 and 99.965%, respectively. They were used as received. After passing through a proper regulator they entered the previously discussed teflon tubing through a Teflon Male Pipe Adapter obtained from Chromatronix, Inc. The helium used was Matheson High Purity grade, 99.995%. After leaving the regulator it passed through a liquid nitrogen gas trap before entering the teflon tubing and going to the reactor.

Vacuum Line

A vacuum was pulled on the reactor by a Pressovac 4 Pump, Cenco, Chicago, Ill. The line connecting the pump with the reactor was supplied with

appropriate traps to prevent contamination of the oil. The vacuum line was connected to the reactor through the previously mentioned pressure line.

Temperature Measurement

Temperature measurement was made inside the reactor by means of a Kel-F coated Copper-Constantan thermocouple. An ice-water reference point was used in conjunction with a Portable Precision Potentiometer, Model 2745, made by Honeywell, Denver, Colorado. The thermocouple was sealed into the reactor using a short length of Chromatronix tubing which was sealed on the outside by clamping and the use of Halocarbon Grease, 25-5S, Halocarbon Products Corp., Hackensack, N. J. After a number of experimental runs it became evident that there was no local heating within the reactor so the thermocouple was removed and the port closed by a teflon plug.

TEMPERATURE CONTROL SYSTEM

The temperature control system consisted of a compressor, expansion valve, cooling coil, constant temperature bath, and control unit. The compressor was made by Lehigh Manufacturing Company, Lancaster, Pa. (Lehigh-Blu Cold Model No. AM42F, FE46) and used Freon 12. The expansion valve was a Detroit Controls Company (Detroit, Mich.) Model 777128, 5-FC. Copper tubing was used to connect the compressor and expansion valve to the cooling coil, which was salvaged from an old refrigerator. To prevent contamination of the ethylene glycol coolant the cooling coil was cleaned and then coated, along with other metal parts except stainless steel, with an epoxy resin supplied by Reichhold Chemicals, Inc., Detroit, Mich. The procedure for coating is given in Appendix I. The temperature bath was a 2.5-gal. fish tank which was modified with two double windows for passage of a light beam, and insulated

with polystyrene foam, Appendix II. The cooling medium was a solution of ethylene glycol and water, 40% ethylene glycol by volume. This had a freezing point of -26°C. Because early work showed some change in transmittance with change in concentration of the ethylene glycol water solutions, as discussed in Appendix III, the coolant was kept at constant concentration by adjustment of the specific gravity according to data found in (71), and listed in Appendix IV. The cooling medium also had to be kept free of foreign matter and color bodies. This was accomplished by cleaning the coolant after each experimental run. The procedure involved passing the coolant through a bed of activated charcoal, then filtering it with a millipore filter of 0.45 μm. pore size (Millipore Filter Corp., Bedford, Mass.) and returning it to the temperature bath. The coolant was circulated by a Teel submersible pump (Dayton Electric Mfg., Chicago, Ill.) with the outlet directed at the edge of the cooling coil. The temperature of the bath was controlled by addition of heat through knife heaters while the compressor continued to operate. A Precision Electronic Relay Control Box No. 62690 (Precision Scientific Co., Chicago, Ill.) was used in conjunction with a Precision Micro-Set Differential Range Thermoregulator ± 0.005°F., -35 to +500°F., to maintain the desired temperature.

PRESSURE MEASUREMENT SYSTEM

The pressure measurement system consisted of a Pace Model P7D, differential type transducer (Whittaker Corp., North Hollywood, Calif.) with a range of ± 15 p.s.i.d. A Pace Transducer Indicator, Model CD25, was used in conjunction with an Esterline Angus recorder (Indianapolis, Indiana) in early work. In later work only the potentiometer circuit of the transducer

indicator was used. A mercury manometer in the system allowed calibration of the transducer before each run, as discussed in Appendix V.

OZONIZER SYSTEM

Myers, et al. (72) and Griggs and Kaye (73) discussed an apparatus for the production of ozone in a quiet electric discharge at the temperature of liquid nitrogen. The principle behind the process was that oxygen at this temperature has a vapor pressure of 162 mm. Hg while that of ozone is 3.5×10^{-3} mm. Hg. Any ozone prepared condensed while liquid oxygen present vaporized to replace the oxygen removed by production of ozone. Eventually the ozone produced was almost free of oxygen. At absolute pressures of less than 50 mm. H_2SO_4 the ozone concentration was greater than 99.9 mole % ozone (74).

The ozonizer system consisted of an ozonizer, an electrical circuit, and a support which holds the ozonizer while it is immersed in liquid nitrogen. Figure 2 is a drawing of the ozonizer. The ozonizer body and the attached stopcocks were prepared by Pope Scientific, Inc. Two-mm. capillary tubing, 1.5-inches long, designed to allow attachment of teflon tubing by special Chromatronix fittings, was fused to the horizontal arms of the stopcocks. The male part of a spherical glass joint, 12/5, was fused to the vertical arm of the three-way stopcock. This allowed attachment of a closed end H_2SO_4 manometer with a vertical leg of 50 cm.

The electrical circuit is shown in Fig. 3. The electrodes are made of 0.005 inch brass shim stock, and are 6-inches long. The electrodes were placed on the ozonizer body in the following manner: the outer electrode was wrapped around the ozonizer body and was held by a spiral spring. The inside electrode was held against the glass by a polystyrene plug which served as

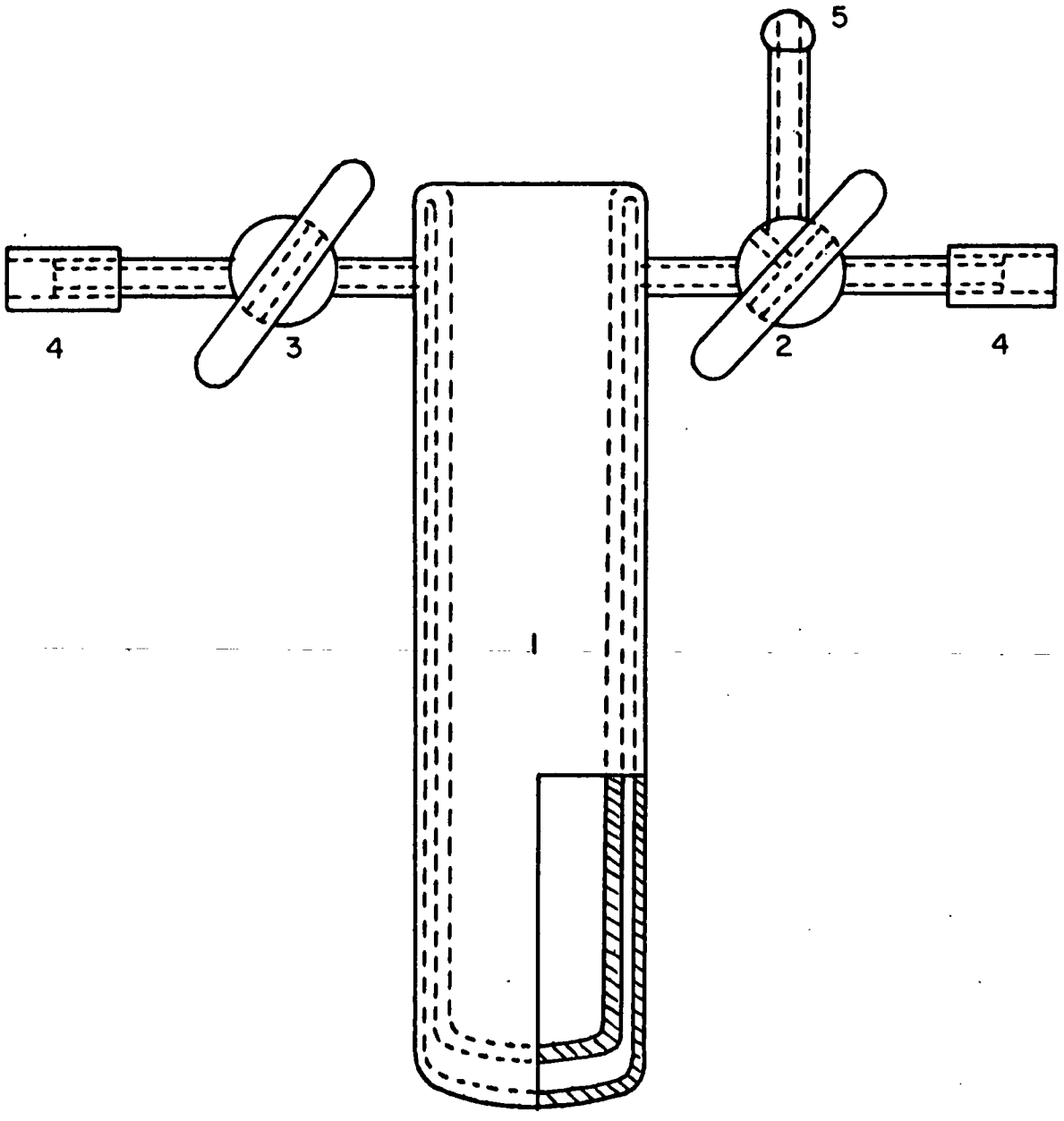


Figure 2. The Ozonizer

1. Ozonizer Body, Prepared by Pope Scientific, Inc. According to Supplied Directions, has 2 mm. Annulus and 9.75 Inch Length
2. 3-Way, 2 mm. Capillary Stopcock
3. 2-Way, 2 mm. Capillary Stopcock
4. Special Chromatronix Fittings for Attachment of Teflon Tubing
5. Spherical Glass Joint for Attachment of H_2SO_4 Manometer

thermal insulation and as a barrier to moisture. To the electrodes were soldered special high voltage wires which were attached to the transformer.

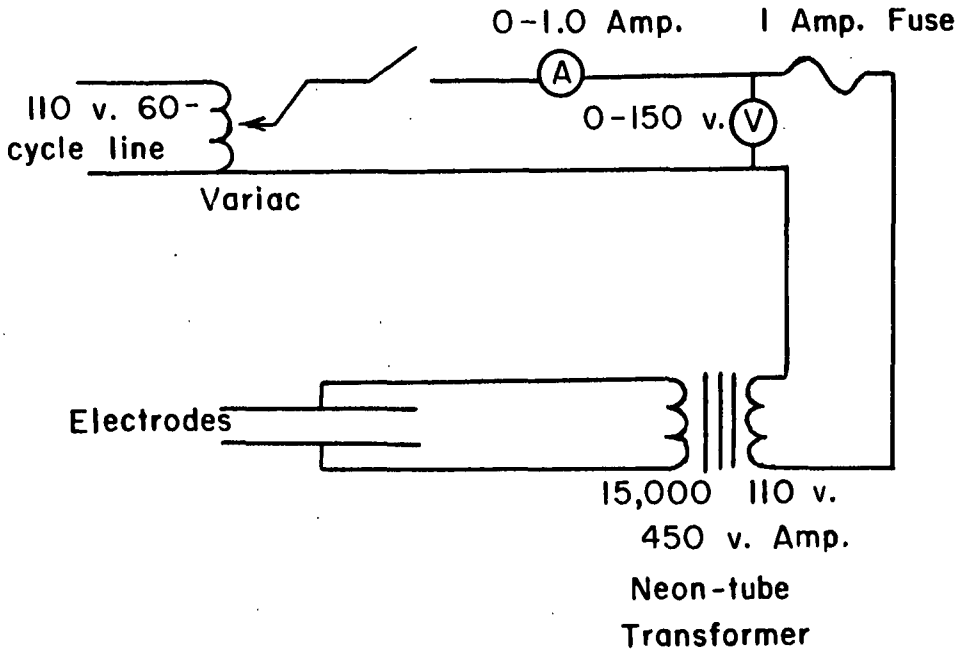


Figure 3. Electrical Circuit for Ozonizer System

The ozonizer support was made of Plexiglas. The ozonizer rested on its arms in grooves on the top surface of the support with the body protruding through and down from the support. Over the top of the ozonizer was placed a small ventilating cap. A circular groove on the bottom of the support allowed a dewar to be placed up against it. A polyethylene curtain extended down from the bottom of the support and encircled the dewar. The dewar was placed in a PVC basket which was raised and lowered by a string and pulley system. The polyethylene curtain fit between the dewar and the basket. During generation of ozone the dewar contained liquid nitrogen. The polyethylene curtain served as a moisture barrier during generation and evaporation of the ozone. During evaporation, when the dewar was lowered, it helped give better temperature control. The assembled ozonizer and support system with the polyethylene curtain and ventilating cap absent is shown in Fig. 4.

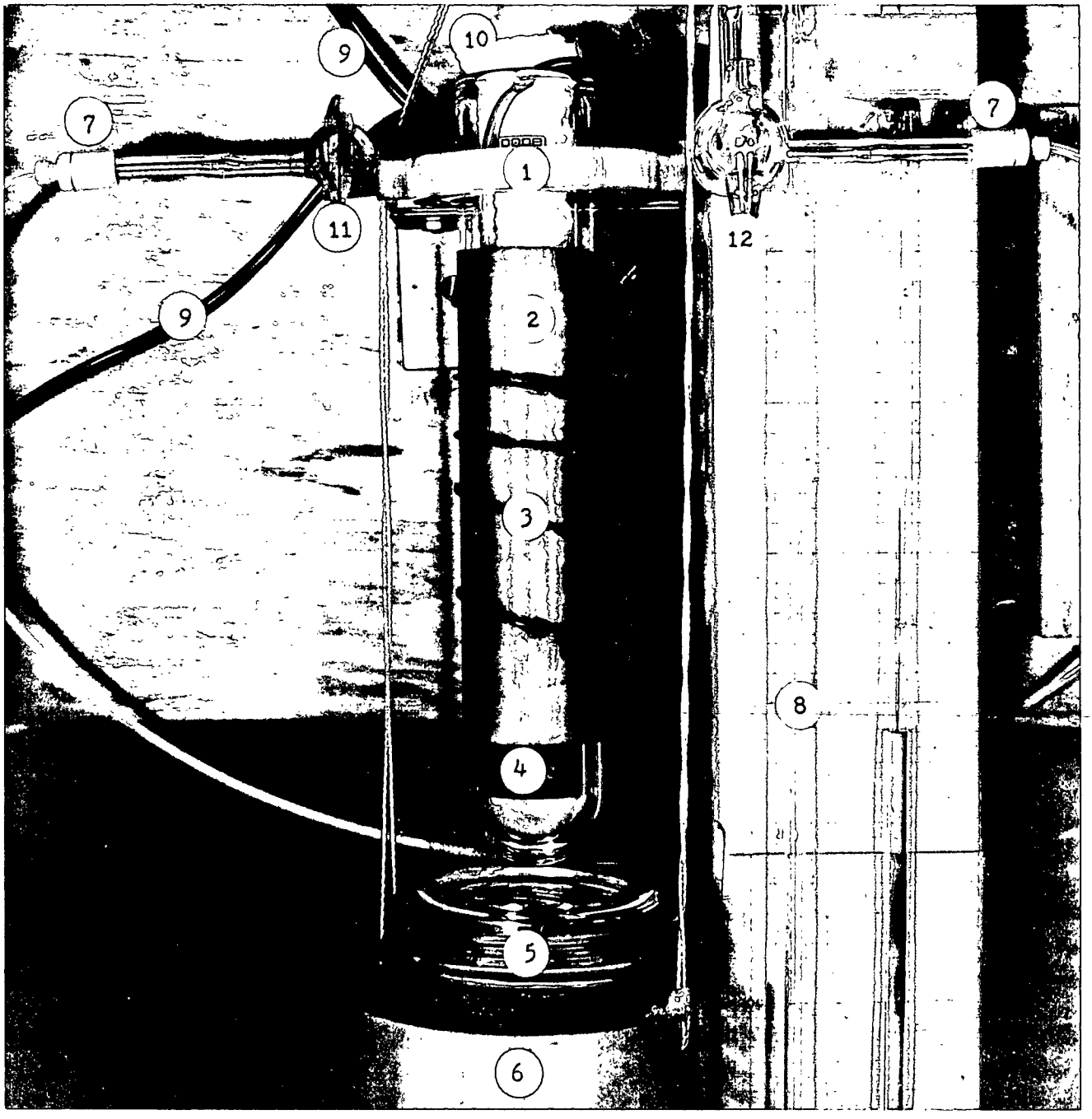


Figure 4. The Assembled Ozonizer and Support System

1. Ozonizer Support
2. Outer Electrode
3. Spiral Spring
4. Inner Electrode
5. Dewar
6. PVC Basket
7. Glass to Teflon Fittings
8. H_2SO_4 Manometer
9. Lead Wires
10. Polystyrene Plug
11. Two-Way Stopcock
12. Three-Way Stopcock

Before use the ozonizer was cleaned with potassium dichromate cleaning solution, and thoroughly rinsed with distilled water. The stopcocks and spherical joints were greased with Halocarbon Grease, 25-5S. The procedure, operating conditions and safety precautions for generation of ozone are given in Appendix VI.

LIGHT ACTIVATION SYSTEM

Lamp Housing

The lamp housing consisted of two metal cylinders, one inside the other. On the top of the inside cylinder was mounted a fan which circulated air down the outside annulus and up through the inside cylinder. This air flow cooled a Hanovia (Engelhard Hanovia, Inc., Newark, N. J.) 673A-10, 550-watt, medium pressure mercury arc lamp which was mounted in the center of the inside cylinder. A 1.0-inch diameter aperture allowed the escape of the light. The electrical leads for the lamp unit went through the walls of both cylinders. The speed of the fan was adjusted by a variac placed in its electrical circuit. The fan was adjusted to give lamp operating conditions of 170 volts, at 4.0 amps. The inside cylinder was made of alzac aluminum, with the bright side toward the light. Figure 5 gives general details of the lamp housing.

Ballast Housing

The ballast housing contained a Hanovia 20651-1, 550-watt ballast system which was compatible with the mercury arc lamp previously discussed. The primary circuit of the ballast was equipped with an on-off switch and a special electrical line capable of delivering 18 amps., at 120 volts during start-up of the lamp. The lamp circuit was equipped with a voltmeter,

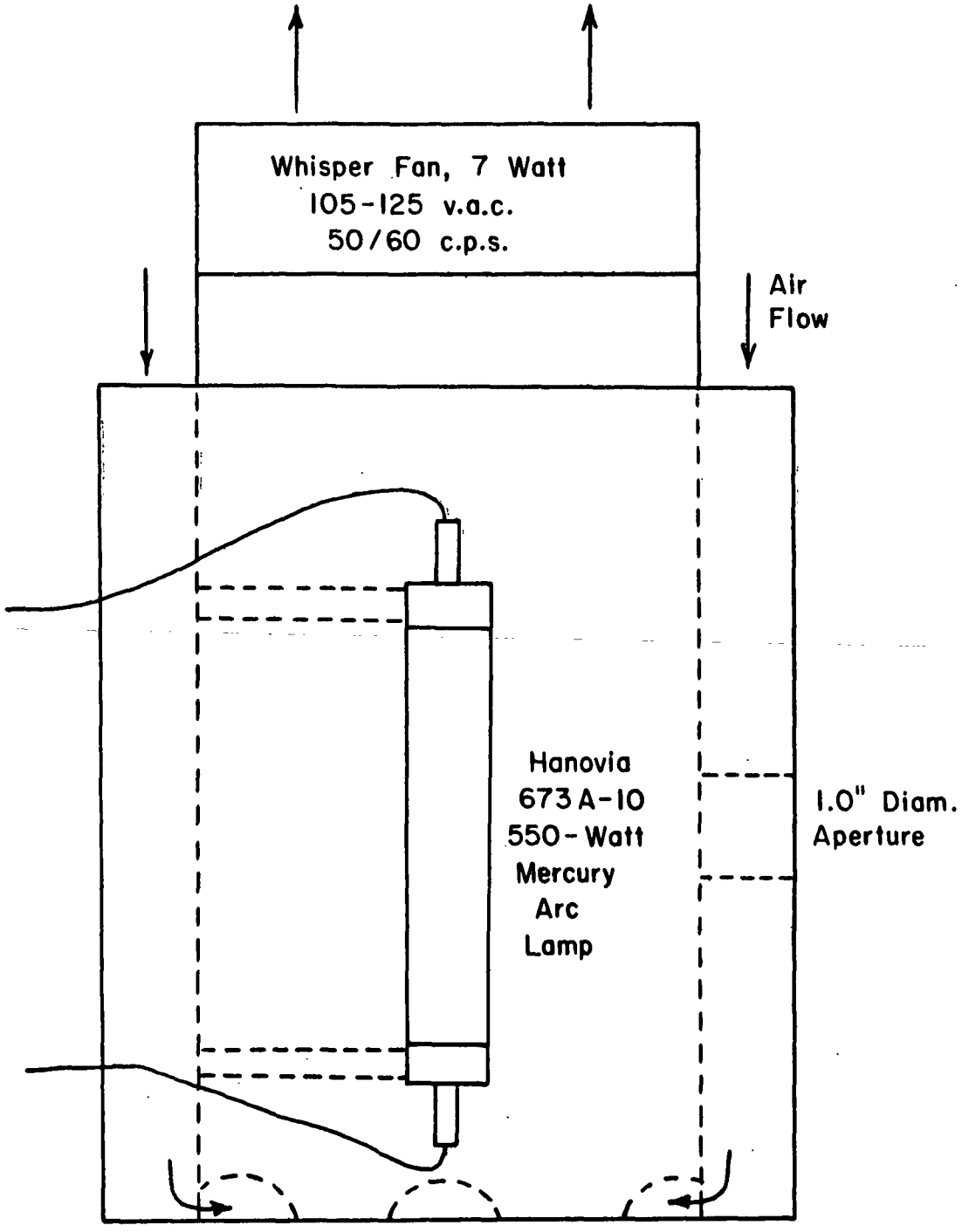


Figure 5. The Lamp Housing

ammeter, fuse, and tickler switch (used to aid starting of the lamp). Figure 6 gives the electrical circuit of the ballast housing.

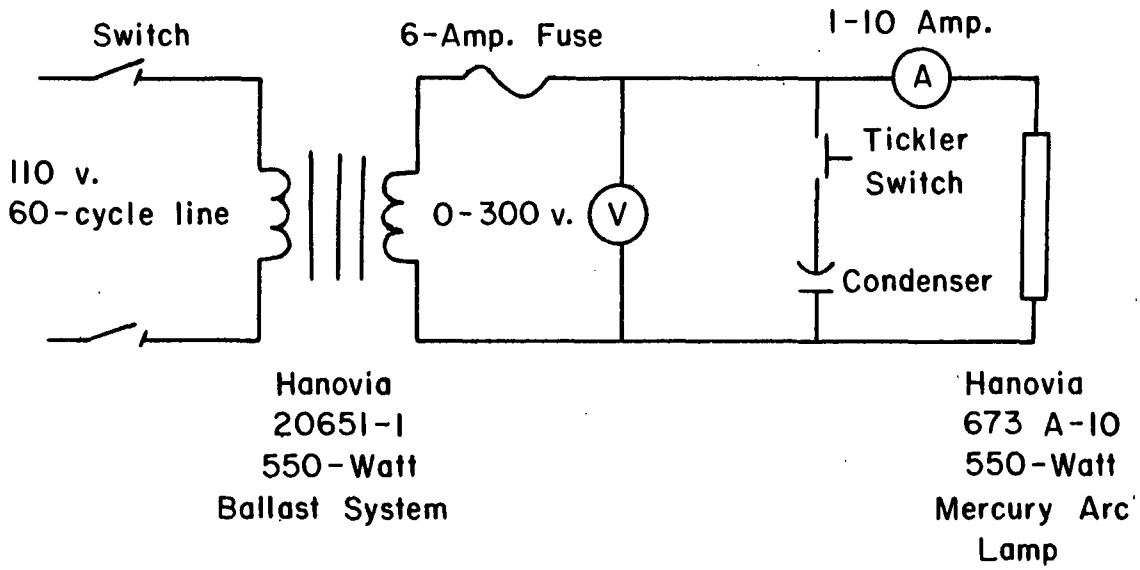


Figure 6. Electrical Circuit of Ballast Housing

Optical Train

The optical train consisted of all elements through which the light beam had to pass before entering the reactor, plus those elements after the reactor which were used to sense the light beam. The lamp was the first element of the train; it was followed by the lamp housing aperture, a 2.5-inch diameter, 2.5-inch focal length lens, glass filters for attainment of light of 365-366.5 nm. wavelength, a 1.0-inch aperture, a window of the temperature bath, ethylene glycol coolant, the reactor, ethylene glycol coolant, a window of the temperature bath, and the sensing elements. Between the filter and stop was placed an on-off shutter. All the elements of the optical train were held in position so that they would not shift from run to run. The glass surfaces were cleaned periodically. The lens was obtained from the physics group of The Institute of

The Densichron system consisted of a meter which was attached to a photocell which had a peak sensitivity in the wavelength range used to activate the photochemical reaction, 365-366.5 nm. The meter was equipped with a scale that could be read in either percentage transmission or optical density. It was equipped with a calibration dial used for zeroing the meter and a range switch with 4 scales. Therefore, if the meter was zeroed at 100% transmission on scale 0, 100% transmission on scale 3 would be equivalent to 0.1% transmission on scale 0.

The chemical actinometer system was used to obtain absolute values of the light intensity. The principle behind the system was that a substance of known photochemical properties was exposed to the light beam whose intensity was to be determined. Because the substance decomposes at a known rate, the light intensity then could be calculated by determining the amount of the substance that decomposed during the time of exposure. The chemical actinometer used in this study was the potassium ferrioxalate system originally studied by Parker (75) and Hatchard and Parker (76) and recommended by Calvert and Pitts (8) in their book "Photochemistry." The theory, preparation, and use of the potassium ferrioxalate actinometer is given in Appendix VII.

EXPERIMENTAL PROCEDURE

The experimental procedure is divided into three parts: the initial procedures, reaction procedures, and recovery of product procedures. The initial procedures discuss those steps needed to get a run ready for starting. The reaction procedures include introduction of reactants, starting the reaction, monitoring, and stopping the reaction. The recovery of products procedures show how this is done.

INITIAL PROCEDURES

These procedures were required before gases could be introduced to the reactor. They are described here in the order in which they are performed. Some of the procedures required several hours to finish, so that other procedures were initiated during these waiting times. These procedures took from 3 to 4 hours to complete. First the refrigeration system was started. This consisted of turning on the compressor, circulation pump, and control unit. The Hg-arc lamp was turned on by closing the switch to the primary circuit of the ballast system; if the lamp did not ignite immediately the tickler switch was closed and then opened after ignition of the lamp. The transducer indicator was turned on. After the voltage in the Hg-arc lamp circuit reached 140 volts, the cooling fan was turned on. The generation of ozone was started as described in Appendix VI. After the Hg-arc lamp had warmed up at least one hour, the reactor was evacuated, and the light intensity was measured as described in Appendix VII, 100 ml. of actinometer fluid was irradiated for 30 min. The solutions to be read on the spectrophotometer were prepared and set aside to be read later. After starting the evaporation of the ozone, the pressure measurement apparatus was calibrated using the procedure given in Appendix V. The chlorine line was then flushed with chlorine into the reactor to remove impurities from this line. The chlorine in the reactor was then pumped out and the reactor rinsed with He or oxygen whichever gas was to be the diluent. This was done by alternately filling and pumping down the reactor. When the reactor was free of chlorine, the shutter was opened and the Densichron photocell placed at the plane of measurement. The Densichron meter was calibrated to read 100% of Scale 0. The shutter was placed in the light beam and the reactor pumped down as far as possible. The system was now ready for introduction of gaseous reactants.

REACTION PROCEDURES

At this stage the temperature bath was at the desired temperature and had been controlling for at least one hour. The Hg-arc lamp had been operating for 3 to 4 hours and the light intensity determined. The shutter was closed and the ozone prepared and evaporated. The Densichron meter and pressure transducer were calibrated. The chlorine line was flushed and the reactor pumped down so that the potentiometer of the transducer indicator read 99.8 to 100. Introduction of reactants was started. Ozone was the first gas to be added. The amount of ozone to be added was first calculated in terms of mm. Hg. This value was then divided by the atmospheric pressure at the time of calibration of the pressure transducer and multiplied by 100. The resultant number was the difference in the potentiometer reading that corresponds to the addition of the desired amount of ozone. This number was then subtracted from the present potentiometer reading, and the potentiometer set at the answer. This caused a deflection of the meter. Ozone was added until the meter approached the zero position. This method of addition was used for chlorine and the diluent. It proved very accurate, usually with less than 0.5 mm. Hg error after final adjustments were made. The ozone was added directly from the ozonizer. The 3-way stopcock was opened so that the teflon tubing between the stopcock and distribution valve into the reactor filled with ozone. (Please refer to Fig. 1, 2, and 4 to see which stopcocks and valves are being discussed.) This length of tubing was previously evacuated. The valve into the reactor was then opened and the ozone allowed to enter slowly while observing the transducer indicator. When the transducer indicator approached the predetermined value, the valve was turned off, and the ozone allowed to come to temperature equilibrium. An adjustment of the potentiometer to zero was made

and the final reading of the potentiometer recorded. The difference between the potentiometer reading before addition gave the amount of ozone or other gas added. After addition of ozone, the 3-way stopcock was closed and the ozonizer body again submerged in the liquid nitrogen. Chlorine was added next through a length of teflon tubing directly from the gas regulator on the cylinder. The amount of chlorine to be added was determined in the same manner as for the ozone. After addition of the chlorine the valves on the regulator and cylinder were immediately turned off. The diluent gas was then added.

The reaction was started by opening the shutter. Just before opening the shutter the following readings were made: transducer indicator potentiometer, atmospheric pressure, amperage and voltage of lamp, scale and percent of scale of Densichron meter and bath temperature. After opening the shutter the same readings were repeated. These readings were repeated at convenient intervals. In early experimental runs the monitoring continued throughout the run while in later experimental runs monitoring during the middle of the run was discontinued. The reaction was stopped after the desired time period by closing the shutter. Final readings were then made.

RECOVERY OF PRODUCTS PROCEDURES

Two methods were used for the recovery of products. The first was used in Experimental Runs 1 through 31. The second was used in Runs 32 through 50. The results of tests on the products recovered by each method were compatible. Both methods used the same recovery apparatus: two 500-ml. gas washing bottles placed in series and connected to the exit port of the reactor. Gas dispersion tubes were attached to the incoming line of the wash bottles by MAN-O-LOK, heat shrinkable teflon tubes (Manostat Corp., New York, N. Y.). The exit tube of the first wash bottle and entrance tube of the second were connected by

heat shrinkable teflon tubing supplied by Pope Scientific, Inc. The connection from the exit port of the reactor to the entrance tube of the first wash bottle was made by Chromatronix tubing and the special teflon to glass fitting. For recovery of products the first wash bottle was filled with 190 ml. of water, and the second with 190 ml. of 0.1N NaOH (190 ml. of 0.1N NaOH was shown to fully trap all chlorine at levels used in the experimental runs).

In Recovery Method One, 250 ml. of precooled carbon tetrachloride (CCl_4) was first added to the reactor through the incoming port for liquids. The method for purification and storage of carbon tetrachloride is given in Appendix VIII. The carbon tetrachloride was precooled to the temperature of the bath by placing it in a 500-ml. round-bottomed flask which was then placed in the bath for 15 min. The carbon tetrachloride in the round-bottomed flask was protected from moisture by a drying tube placed in a rubber stopper in the flask. A glass and teflon tubing connection was also placed through the stopper so that the carbon tetrachloride could be withdrawn from the round-bottomed flask into the reactor while the flask remained in the temperature bath. Since the reactor in all runs was at pressure less than atmospheric, the carbon tetrachloride was forced into the reactor upon opening the incoming port. The reactor was then thoroughly rinsed with the carbon tetrachloride by removing the reactor from the temperature bath and shaking it vigorously. This helped dissolve the chlorine, ozone, and reaction products. The carbon tetrachloride at this point took on a noticeable blue color from the ozone; it was evident from observation of this color that in longer runs there was less ozone remaining. After thoroughly rinsing the reactor it was placed back into the bath at an angle so that the opening of the exit tubing was at the lowest point. The reactor was pressurized by the addition of He. The exit port was then opened and the carbon tetrachloride forced into the wash

bottle containing water. After the carbon tetrachloride was in the wash bottle, purging with He through the reactor was continued for 30 min. The rate of purging was such that there was a froth of bubbles at the water surface. The blue color of ozone in the carbon tetrachloride disappeared after 5 min. to be replaced by the yellow color of chlorine which disappeared after 15 min. The last 10 min. of purging was done while the carbon tetrachloride was colorless. After purging was completed the helium stream was shut off. The water and carbon tetrachloride layers in the first wash bottle were separated. The carbon tetrachloride was extracted several times with a small portion of water and this water added to the water material already obtained. The carbon tetrachloride was then saved to be purified for later use. The water material was labeled CCl_4-extraction material, diluted to 250 ml. with water in a volumetric flask, and stored for analysis. The material in the second wash bottle, which originally contained 190 ml. of 0.1N NaOH was diluted with water in a 250-ml. volumetric flask, labeled 0.1N NaOH material, and stored for analysis. The inside of the reactor body was then rinsed with four 20-ml. portions of water. This material was diluted to 100 ml. with water, labeled reactor rinse material, and stored for analysis. During the time required to recover the products the Hg-arc lamp, refrigeration system, and pressure measurement system were turned off. The final step was to purge the now wet reactor with dry helium to dry out the reactor, then pump down the reactor to further dry it out.

In Recovery Method Two the introduction of carbon tetrachloride to the reactor was eliminated. The reactor was purged with helium, for at least 30 min., or until the odor of ozone at the exit was negligible, directly into the first wash bottle containing 190 ml. of water and the second containing 190 ml. of 0.1N NaOH. The material recovered in the first wash bottle was labeled

water wash material, and diluted to 250 ml. The material from the second wash bottle was labeled 0.1N NaOH material and diluted to 250 ml. The reactor was then rinsed and dried as in the first method. The storage of all products was done at room temperature in the dark.

ANALYTICAL PROCEDURES

Five analytical procedures were adopted from the current literature to allow the analysis of aqueous mixtures of chloride, hypochlorite, chlorite, chlorate, and perchlorate. Modifications were made to the procedures to make them more applicable. Each procedure used colorimetry to determine the concentration of desired species. A more detailed description of each procedure, along with the calibration curves obtained, is given in Appendix IX.

ACCURACY OF PROCEDURES

After each analytical procedure was established, a mixture containing known amounts of chloride, hypochlorite, chlorite, chlorate, and perchlorate was prepared. This mixture was then analyzed using the five analytical procedures every day over a period of five days. The data obtained gave an idea of the accuracy of the analytical procedures and the stability of the mixture when stored at room temperature in the dark. Table II presents these data. It was obvious that the mixture remained stable over the five-day period. The data also indicated the accuracy of the test: Test A, ± 3.0%; Test B, ± 5.0%; Test C, ± 3.0%; Test D, ± 6.0%; and Test E, ± 9.0%. The stability of the mixture indicated that full analysis of products does not have to be made immediately after each run.

TABLE II

ACCURACY OF ANALYTICAL TESTS AND STABILITY OF MIXTURES OF IONIC CHLORINE COMPOUNDS

Test	Species Tested	Known	Date of Test 4/7/70	4/8/70	4/9/70	4/10/70	4/11/70
A	ClO^-; equiv. x 10^6/ml.	1.82	1.84	1.88	1.78	1.85	1.82
B	ClO^-,ClO_2^-; equiv. x 10^6/ml.	2.29	2.31	2.40	2.36	2.25	2.17
C	ClO_2^-,ClO_3^-; equiv. x 10^6/ml.	1.48	1.45	1.44	1.53	1.52	1.55
D	ClO_4^-; moles x 10^6/ml.	0.74	0.77	0.80	0.85	0.76	0.70
E	ClO^-,ClO_2^-,Cl^-; moles x 10^6/ml.	2.64	2.41	2.47	2.97	2.85	2.58

SCHEDULING OF ANALYSIS

As noted previously, each experimental run produced three solutions which were analyzed for every product. Therefore, to save time the maximum amount of samples were run in each separate test made. This required making several experimental runs before analysis of the samples were made. For example, Test D was set up so that ten samples and two blanks were run for each separate test. The test was not run unless there were ten samples to be tested.

RESULTS AND DISCUSSION

This section discusses necessary preliminary work which was required before actual experimental runs could be made. It presents a description of the products formed upon analysis of the reaction products. It presents results obtained due to variation of selected parameters of the reaction. It develops a proposed reaction mechanism for the system studied and discusses the results in relation to certain literature contradictions.

PRELIMINARY WORK

Certain preliminary work was required in order (1) to establish the method for determining the light intensity inside the front surface of the reactor by use of a reading outside the reactor, (2) to measure the purity and stability of the ozone added to the reactor, and (3) to show that the final ozone concentration could not be determined by chemical methods.

LIGHT INTENSITY, ABSORPTION, MEASUREMENT, AND STABILITY

The optical train used in the experimental work has already been described. Figure 7 presents a simple diagram of the optical train. However, this optical train is not normal because the light beam produced is divergent. Upon entering the reactor with a diameter of 1.0 inch the light beam forms a cone and strikes the sides of the reactor approximately 3 inches from the inside front surface. The divergent beam was necessary in order to have a light intensity at a level, 10^{15} quanta/sec., where runs could be made in 4 hours with detectable product formation ($>10^{-6}$ moles). In preliminary work, a parallel beam was used. However, with the lenses available the light intensity obtained was of the order of 10^{14} quanta/sec. Experimental runs at this

light intensity would have required excessive reaction times, 20 to 30 hours, for formation of a detectable amount of product.

Because the light beam was divergent it became necessary to absorb all the light entering the reactor. If it was not all absorbed, there would be no manner in which to detect how much was absorbed. Therefore, in all runs the concentration of chlorine (8.82×10^{-3} mole/liter) was such that essentially all of the light entering the reactor was absorbed. This was shown by calibrating the Densichron meter before each run to 100% of scale zero. When chlorine was added to the reactor at the above concentration the Densichron reading became 5.0% of Scale 3 or 0.005% of Scale 0. This indicates that 99.995% of the straight-through light was being absorbed. Therefore, it was assumed that under these conditions all of the light entering the reactor was absorbed.

In order to determine the light intensity at the inside front surface of the reactor, a bath factor was determined that related the light intensity at the plane of measurement to that at the inside front surface of the reactor. The use of this predetermined bath factor necessitates that all optical surfaces are kept clean, that all liquids in the optical train remain pure, and that the optical train does not shift. All of these precautions were taken.

The bath factor was determined in the following manner. The optical train was prepared as if an experimental run was to be made. The reactor was placed in its position in the temperature bath and the precautions mentioned above were taken. The mercury arc lamp was allowed to warm up for one hour. The light intensity was measured using the liquid actinometer system at the plane of measurement. The actinometer liquid was introduced into the reactor and the light intensity at the front surface of the reactor was measured.

The procedures for measuring and calculating the light intensity are given in Appendix VII. After each individual test to determine the bath factor the reactor was rinsed thoroughly with water and dried. The ratio of the light intensity inside the reactor to the light intensity at the plane of measurement is the bath factor. Therefore, during experimental runs the light intensity at the plane of measurement could be determined and by multiplication by the bath factor the light intensity at the inside front surface of the reactor established. Table III presents the data used to determine the bath factor and the value obtained for the bath factor.

TABLE III

DATA USED FOR DETERMINATION OF THE BATH FACTOR

Date Data Obtained	Light Intensity, quanta/sec. (10^{-15})		Bath Factor
	Inside Reactor	At Plane of Measurement	
1/15/71	4.670	2.511	1.860
1/18/71	4.641	2.479	1.872
1/18/71	4.713	2.543	1.853
1/19/71	4.771	2.588	1.844
1/20/71	4.641	2.479	1.872
		Average	1.860
		Standard Deviation	0.0122
		95% Confidence Limits, t-test	±0.014
		Value of Bath Factor to be Used	1.86 ± 0.01

The determination of the bath factor allowed the determination of the light intensity inside the reactor by measuring the light intensity at an external point. However, this measurement had to be made before an experimental run was started. There was the question of the stability of the Hg-arc lamp

and the resultant light intensity produced. If the light intensity of the lamp fluctuated during the period of a run this could cause errors in the calculations of total quanta absorbed. Data were taken at three different times on 1/15/71, 9:30 a.m., 2.51×10^{15} quanta/sec.; 1:30 p.m., 2.49×10^{15} quanta/sec.; 7:30 p.m., 2.55×10^{15} quanta/sec.; thus, fluctuation of the intensity is not a problem.

OZONE, PURITY, AND STABILITY

The apparatus to produce ozone has been described earlier. The procedure, operating conditions, and safety precautions for generation of ozone are given in Appendix VI. Although the ozone prepared was supposed to be 99.9% pure, there was the possibility that the ozone would decompose when it was evaporated and introduced into the reactor. Therefore, an experiment was devised to measure the purity of the ozone.* Table IV shows the results of two trials made to determine ozone purity. It appears that within experimental accuracy the ozone introduced into the reactor can be considered 100% pure.

*Ozone was prepared in the ozonizer, and was evaporated. The evaporated material was introduced into the reactor, which was maintained at a constant temperature, and the pressure change was recorded. The gas added to the reactor was then purged from the reactor with He at a predetermined rate for 30 min. into a train of two 500-ml. gas washing bottles each containing 190 ml. of 0.1N NaOH and 5 grams of KI. The material in each wash bottle was diluted to 250 ml. in a volumetric flask. A 25-ml. aliquot was then acidified by 50 ml. of 0.1N H_2SO_4 containing KI and the liberated iodine titrated with 0.1N thiosulfate. The moles of ozone were then calculated. The number of moles of ozone by titration was then checked with the number of moles of gas added to the reactor.

TABLE IV

PURITY OF OZONE ADDED TO THE REACTOR

Date Data Acquired	Moles of Gas Added to Reactor	Moles of Ozone Recovered
8/5/71	$3.41 \pm 0.02 \times 10^{-3}$	$3.36 \pm 0.04 \times 10^{-3}$
8/9/71	$3.63 \pm 0.02 \times 10^{-3}$	$3.69 \pm 0.04 \times 10^{-3}$

The stability of the ozone was also of concern since thermal and photochemical decomposition during an experimental run would further complicate the system. Calculations using literature data (77) showed that at 0°C. the thermal decomposition of ozone would be negligible and undetectable by the pressure measurement system. A paper by Griggs (78) indicates no absorption of 365-366.5 nm. light by ozone. Experimental work with ozone added to the reactor showed no increase in pressure at -5°C. due to thermal or photochemical decomposition. The pressure was monitored with a H_2SO_4 manometer for 2.5 hours in each case. Further experimental work with ozone and helium in the reactor at 0.0°C. at a light intensity of 1.73×10^{15} quanta/sec. showed a pressure increase over 10 hours of 1.7 mm. Hg. The starting total pressure was 449.5 mm. Hg of which 106.3 was due to ozone and 343.5 due to He.

SEPARATION OF OZONE AND CHLORINE

The analytical techniques which have been explained previously allow a complete analysis for ionic chlorine species. However, no mention has been made of the analysis of the product gases for the remaining ozone in the system. Two methods were attempted in which it was hoped that the final ozone concentration could be established; both were failures. The first attempt involved trapping the ozone in 0.1N NaOH containing KI. However, prior to this, all

chlorine species had to be removed so that the gas stream first had to be scrubbed in 0.1N NaOH. This proved unacceptable since the ozone partially decomposed in the 0.1N NaOH material.

A second method was tried which attempted to separate the chlorine from the ozone by condensing the chlorine in a cold trap while the ozone passed through to be trapped in a wash bottle containing 0.1N NaOH and KI. The temperature used was that of melting pentane, -129°C. At this temperature, chlorine has a vapor pressure of less than 1.0 mm. Hg and ozone has a vapor pressure in excess of 100 mm. of Hg. A flow rate of purging gas was established which worked successfully when the gases were pure, i.e., chlorine was trapped, and ozone was fully purged through. However, when the two gases were placed together and separation attempted it was found that there was a holdup of ozone in the condensed chlorine so that separation was not complete.

INTERESTING SIDELIGHTS

During the work that was done to see if ozone could be separated from chlorine in a wet process some interesting phenomena were encountered. Although they were not pursued fully they are presented here so that the knowledge will not be lost.

First, when helium or oxygen are bubbled through mixtures of hypochlorite, chlorite, and chlorate, for 30 minutes at a pH of 8.5 and room temperature, the solutions are left unchanged (Table V).

TABLE V

EFFECT OF BUBBLING He AND O_2 THROUGH A SOLUTION CONTAINING ClO^-, ClO_2^-, AND ClO_3^-

	1st Analysis, moles/ml. (10^6)			2nd Analysis[a], moles/ml. (10^6)		
	ClO^-	ClO_2^-	ClO_3^-	ClO^-	ClO_2^-	ClO_3^-
Untreated	0.401	0.014	0.189	0.411	0.012	0.197
Treated with He	0.405	0.021	0.183	0.401	0.026	0.186
Treated with O_2	0.412	0.015	0.189	0.413	0.019	0.193

[a]The second analysis occurred four days after the first.

Second, when ozone is bubbled into a solution of hypochlorite, chlorite, and chlorate under the above conditions the hypochlorite is destroyed, chlorate is produced, and chlorite remains unchanged. The chlorate produced does not account for all of the hypochlorite destroyed so it is assumed that the rest of the hypochlorite destroyed goes to chloride. It appears that the ozone is accelerating the two known reactions for the breakdown of hypochlorite.

$$3\ ClO^- \longrightarrow 2\ Cl^- + ClO_3^- \qquad (86)$$

$$2\ ClO^- \longrightarrow 2\ Cl^- + O_2. \qquad (87)$$

Equation (86) does not account for all of the hypochlorite destroyed so Equation (87) must also take place. Since this work has also shown that the ozone itself decomposes in 0.1N NaOH, the decomposition must be quite complex. Table VI presents the data considered.

The third phenomenon occurred when a trace of KI was added to a neutral solution of hypochlorite. Subsequent bubbling with He and oxygen for 30 min. at room temperature produced solutions containing no hypochlorite and a substantial increase in the chlorite species; Table VII presents the data.

TABLE VI

EFFECT OF BUBBLING O_3 THROUGH SOLUTIONS CONTAINING ClO^-, ClO_2^-, AND ClO_3^-

	Species, moles/ml. (10^6)		
	ClO^-	ClO_2^-	ClO_3^-
Untreated	0.486	0.027	0.209
Treated	0.0	0.027	0.299
Untreated	0.669	0.004	0.015
Treated	0.0	0.018	0.116

The explanation of the phenomenon is based on the pH of 6.5. At this pH the residue of KI would not react with the chlorite formed. Breakdown of hypochlorite to chloride and chlorate is believed to follow the mechanism

$$HClO + ClO^- \longrightarrow HClO_2 + Cl^- \quad (88)$$

$$ClO^- + HClO_2 \longrightarrow HClO_3 + Cl^-. \quad (89)$$

If Equation (88) is accelerated then there is a possibility of obtaining a solution high in chlorite content with no hypochlorite present. It was suggested (79) that the KI accelerates Equation (88) by acting as a catalyst as it does in some organic reactions.

$$HClO + H^+ + 2\,I^- \longrightarrow Cl^- + H_2O + I_2 \quad (90)$$

$$I_2 + H_2O \longrightarrow H^+ + I^- + HIO \quad (91)$$

$$ClO^- + HOI \longrightarrow I^- + HClO_2 \quad (92)$$

$$HClO + ClO^- \longrightarrow HClO_2 + Cl^-. \quad (88)$$

This mechanism could explain the formation of chlorite from hypochlorite at the pH of 6.5.

TABLE VII

PRODUCTION OF ClO_2^- FROM ClO^- IN THE PRESENCE OF A TRACE OF KI AT pH 6.5

		Species, moles/ml. (10^6)		
		ClO^-	ClO_2^-	ClO_3^-
O_2 Used for bubbling	No KI added	0.672	Trace	Trace
	KI added	0.0	0.371	Trace
He Used for bubbling	No KI added	0.634	Trace	Trace
	KI added	0.0	0.359	Trace

PRODUCTS OF THE REACTION

The following will describe what ionic chlorine species were found in each of the three solutions obtained from an experimental run. Chlorine material balances will be presented based on a complete analysis of the solutions and on an estimate of the chloride present in the solutions.

IONIC CHLORINE SPECIES FOUND

As described earlier, each experimental run produced three aqueous solutions which had to be tested for the five ionic chlorine species: hypochlorite, chlorite, chlorate, perchlorate, and chloride. These solutions were called the reactor rinse material, the CCl_4-extraction or water wash material, and the 0.1N NaOH material. After a number of trial and experimental runs it was found that certain ionic chlorine species were found exclusively in one sample while others were found in all the samples. The concentrations of ionic chlorine species are expressed in terms of moles/ml. of solution in which they are found.

The species found in the reactor rinse material were perchlorate, hypochlorite, and chloride. No significant amounts of chlorite were ever found.

Chlorate was found at a level less than 0.005×10^{-6} moles/ml. The amounts of hypochlorite and chloride found were small (0.10×10^{-6} moles/ml.) and were assumed to be the result of residual chlorine present in the reactor after the purging with He was completed. Perchlorate was assumed to be produced by the breakdown of a chlorine oxide product of the reaction. Except for Runs 1, 2, and 3, perchlorate was always found in the reactor rinse material and the amount found varied according to the length of time of the run and to the amount found in the water wash or CCl_4-extraction material, with the maximum being 3.6×10^{-6} moles/ml.

The species found in the water wash or CCl_4-extraction material were hypochlorite, chloride, and perchlorate. No significant amounts of chlorite were ever found. Chlorate was found at a level less than 0.5×10^{-6} moles/ml., and is assumed to be a product of the hypochlorite disproportionation reaction. The hypochlorite and chloride (0.615 to 3.3×10^{-6} moles/ml.) were assumed to come from chlorine dissolved in the water. The perchlorate found (0 to 1.085×10^{-6} moles/ml.) in this solution came originally as a material dissolved in carbon tetrachloride or in the gas stream. In both cases it was originally a chlorine oxide product of the reaction.

The species found in the 0.1N NaOH material were hypochlorite, chloride, and chlorate. No chlorite or perchlorate were found. Hypochlorite and chloride (up to 34.9×10^{-6} moles/ml.) were the major species found because the 0.1N NaOH solution would trap all remaining free chlorine. The chlorate (0.08 to 0.68×10^{-6} moles/ml.) is assumed to be a product of the hypochlorite disproportionation reaction. In light of an earlier section that discussed how ozone can accelerate the breakdown of hypochlorite to chlorate and chloride it is to be expected in this solution.

It appears that the only ionic chlorine species found in these solutions that can be linked to a chlorine oxide product of the reaction is perchlorate. The presence of chloride, hypochlorite, chlorite, and chlorate also could be linked to specific chlorine oxide products. However, the chloride, hypochlorite, and chlorate found have been attributed to the chlorine remaining in the system and chlorite has not been found in quantities greater than 10^{-8} moles/ml. However, the presence of chlorine oxides which form chloride, hypochlorite, chlorite, and chlorate in water has not been ruled out. These chlorine oxides are considered to be present at concentrations too low to be detected by the wet analytical methods used.

To save time in the analysis of solutions the analysis of some solutions for selected species was eliminated after general trends were established. Therefore, for most experimental runs no chloride analysis was made on any of the three solutions. The perchlorate analysis was eliminated on the 0.1N NaOH material as were the hypochlorite and chlorite analyses.

CHLORINE MATERIAL BALANCE

A chlorine material balance was made in order to establish the efficiency of trapping the chlorine compounds produced in the reaction and the chlorine that remained unreacted. A complete analysis of the three samples from Trial T-28-O_3 was made; these data can be found in Appendix X. The data indicate that 94.7% of the chlorine added was accounted for by the analytical procedures. The error is most likely due to Test E, which measures total moles of chloride, hypochlorite, and chlorite present in each sample. As previously discussed this test has an accuracy of ± 9.0%. Since the majority of the chlorine is trapped as hypochlorite and chloride it is expected that the error of the total chlorine material balance would reflect the error of determination

of total hypochlorite, chlorite, and chloride. Therefore, in Trial T-28-O_3 the amount of chlorine accounted for by the analytical procedures is within the range of error expected.

A method was used to obtain an estimated material balance when Test E was not run. The amount of chloride present in each sample was estimated based on the amount of hypochlorite and chlorate present in the sample. Since a chlorine molecule breaks down in water to form one molecule of hypochlorite and one of chloride, it was assumed that the amount of chloride present was at least as much as the hypochlorite. Furthermore, in the hypochlorite disproportionation reaction,

$$3\ ClO^- \longrightarrow 2\ Cl^- + ClO_3^-, \qquad (86)$$

three moles of hypochlorite break down to form two of chloride and one of chlorate. Therefore, since it is assumed that the chlorate found is due to Equation (86), the amount of chlorate found was doubled and this amount added to the estimate of chloride in the sample. An estimate of the total amount of chlorate found in the 0.1N NaOH material had to be made for a large number of the runs. This estimate was taken as 0.05×10^{-3} moles of chlorate and was based on an average of $0.055 \pm 0.011 \times 10^{-3}$ moles of chlorate found for 26 acceptable experimental runs (R-1 through R-30). This technique of obtaining a material balance still did not fully account for all of the chlorine introduced as can be seen in Appendix X. The average of 18 separate material balances was 94.8% recovery. The range was 88.0 to 101.3%. The discrepancy is caused by unaccounted chloride. As discussed earlier, ozone accelerates the decomposition of hypochlorite. It appears that it does this by accelerating both Equations (86) and (87),

$$3\ ClO^- \longrightarrow 2\ Cl^- + ClO_3^- \qquad (86)$$

$$2\ ClO^- \longrightarrow 2\ Cl^- + O_2. \qquad (87)$$

Since there is no way to estimate the amount of chloride produced by Equation (87) there is a negative discrepancy in the material balance.

It is also of interest to note the closeness of the material balances obtained for T-28-O_3 when total analysis is made and when the estimation technique is used; respectively these are 94.7 and 92.7% recovery.

UNITS USED IN DATA PRESENTATION

One characteristic of a photochemical system is that the light intensity of the beam decreases as it passes through the reactor. In the case under study, an estimated 90% of the light is absorbed in the first two inches of the reactor. Therefore, there is the possibility of having locally high concentrations of products and intermediates in the front portion of the reactor while other portions of the reactor have relatively low concentrations of products and intermediates. This causes problems in the interpretation of product and intermediate concentrations. If concentrations are expressed one must realize that this in effect would be an average concentration of the material over the whole volume considered. In the presentation of data in the following sections, the perchlorate formed from chlorine oxide products of the reaction will be expressed in terms of total moles formed over the time period of the reaction. If one wishes to express this in terms of concentration, the volume of the reactor used in the study is 0.6116 liter.

That volume of the reactor where most of the light is absorbed is where the major portion of the reaction takes place since the chlorine atom concentration is maintained at a significant level. This volume will be called the

reaction zone and is estimated to be 0.155 liter. The reaction zone is based on the first 3 inches of the reactor having a diameter of 2 inches because, as noted previously, 90% of the light is absorbed in the first 2.0 inches of the reactor and the divergent light beam strikes the wall of the reactor 3.0 inches after entering. In later calculations the equilibrium concentration of chlorine atoms and other intermediates, and the rate of formation of chlorine oxide products, will be based on the volume of the reaction zone. Since diffusion calculations, Appendix XI, show that the concentration of reactants, diluents, and products will be essentially the same throughout the reactor, the concentration of reactants, diluents, and chlorine oxide products will be expressed in terms of the entire reactor volume, 0.6116 liter.

PARAMETERS OF THE REACTION

As noted previously, perchlorate is the only ionic chlorine species found which can be directly related to stable chlorine oxide products of the reaction. Because of this, the following section will present the data obtained in the experimental program based on the amount of perchlorate found. Seven parameters will be presented: light intensity, time, temperature, third bodies, ozone concentration, total pressure rise in the system during reaction, and quantum yield. Interpretation of the results will be based on knowledge of general photochemical systems. The use of these data in developing a proposed reaction mechanism and the contradiction between these data and present accepted literature will be discussed in later sections.

LIGHT INTENSITY DEPENDENCE

Experimental runs were made at -10.5 and 0°C. with various levels of light intensity and reaction time. At -10.5°C. the equimolar reactant

concentrations for chlorine, ozone, and helium were $9.15 \pm 0.05 \times 10^{-3}$ each and at 0°C. they were $8.82 \pm 0.05 \times 10^{-3}$ moles/liter each. Table VIII presents the data obtained. Figures 8 and 9 present the plotted data for -10.5 and 0°C., respectively, for moles of perchlorate formed versus light intensity at constant reaction time. These figures indicate that the formation of perchlorate is directly proportional to the light intensity. The data taken at -10.5°C. does not show this well because the light intensities are not scattered enough. However, the data taken at 0°C. show this trend well, especially that for runs of 10 hours. Table IX presents the data obtained at 0°C. grouped into three light intensity levels through the use of a direct proportion. Figure 10 presents the plotted data, adjusted moles of perchlorate versus time of reaction at constant light intensity. A direct proportionality between formation of perchlorate and time at constant light intensity is indicated. Because of this direct relationship, under the reaction conditions studied, all data can be corrected to the same base light intensity. The base light intensity was chosen as 3.05×10^{15} quanta/sec. (this was approximately the average for the experimental runs at -10.5°C.). All of the data presented in later sections are corrected to this base level.

Calvert and Pitts (8) indicate that the intensity dependence of a product rate can help to establish whether a product is formed in a primary process (directly related to the absorbed quantum of energy) or a secondary process (thermal reaction following primary process). The rates of products formed in primary processes are directly proportional to the absorbed light intensity. The rates of products formed in secondary reactions are usually other than directly proportional. However, there are some cases where products formed in secondary reactions are directly proportional to the light intensity.

TABLE VIII

EFFECT OF LIGHT INTENSITY ON PRODUCTION OF ClO_4^-

Data for -10.5°C.				Data for 0°C.			
Time of Run, hr.	Run	Light Intensity, quanta/sec. (10^{-15})	ClO_4^- Formed, moles (10^4)	Time of Run, hr.	Run	Light Intensity, quanta/sec. (10^{-15})	ClO_4^- Formed, moles (10^4)
4	5	3.15	0.04	4	20	2.27	0.52
	7	2.83	0.75		23	3.23	0.41
	9	2.95	0.35		49	3.89	1.34
	12	3.04	1.31	7	21	2.05	0.62
	15[a]	2.41	0.81		22	2.96	0.49
	17	2.20	0.39		27	3.28	1.04
8	1	3.48	1.31		50	3.62	1.72
	2	3.65	1.53	10	24	3.46	1.51
14	8	3.09	2.50		28	3.23	1.31
	11	3.11	2.27		33	1.65	0.65
20	6	3.12	2.98		36	1.99	0.83
	10	3.06	3.03		39	3.94	1.91
26	13	2.76	3.20	15	26	3.44	2.44
					47	4.27	3.32
				20	25	3.33	3.61
					46	4.19	4.23
				26	48	4.19	5.11

[a] Not used because of reactor contamination.

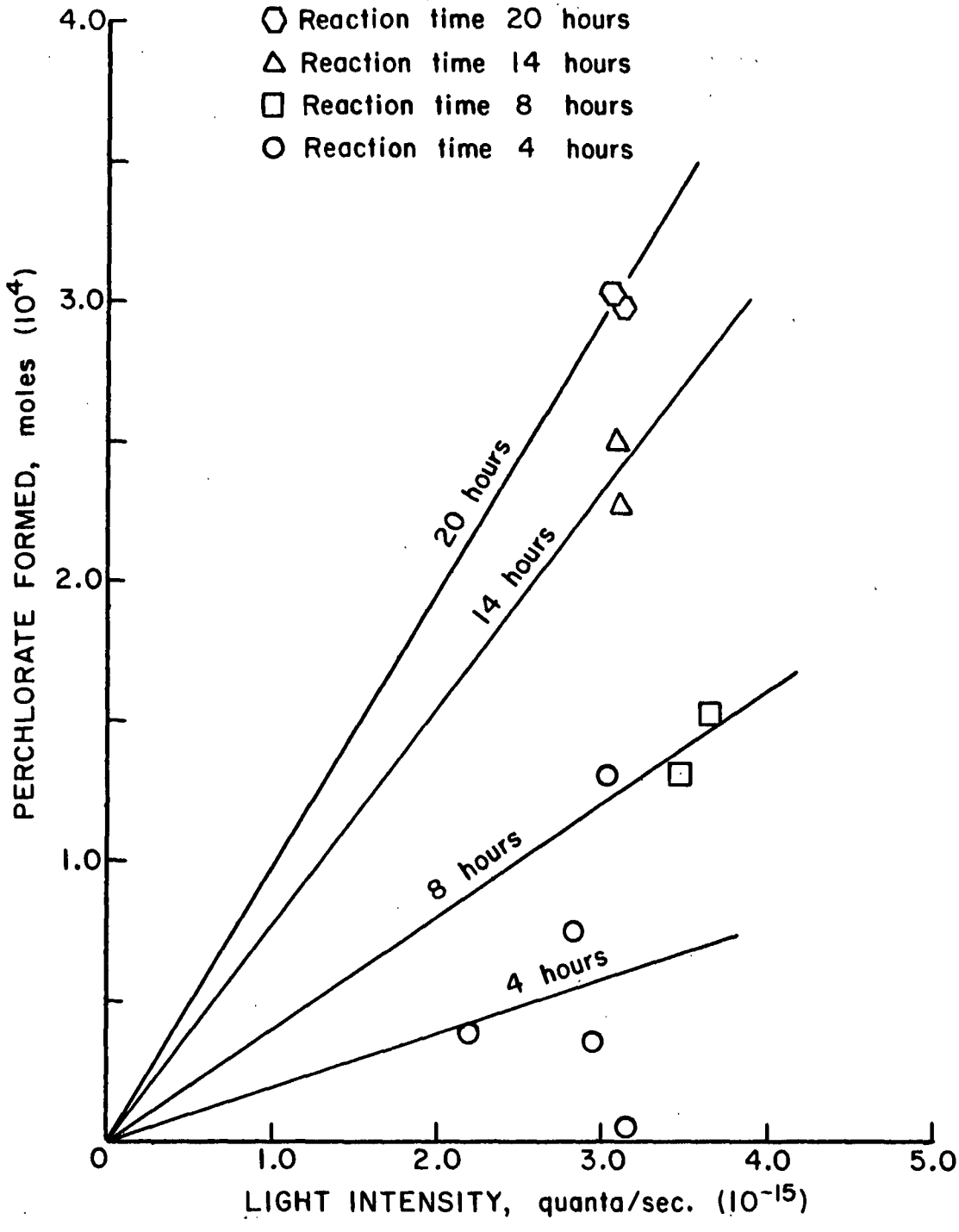


Figure 8. Moles of Perchlorate Formed vs. Light Intensity at Constant Time and Temperature of -10.5°C.

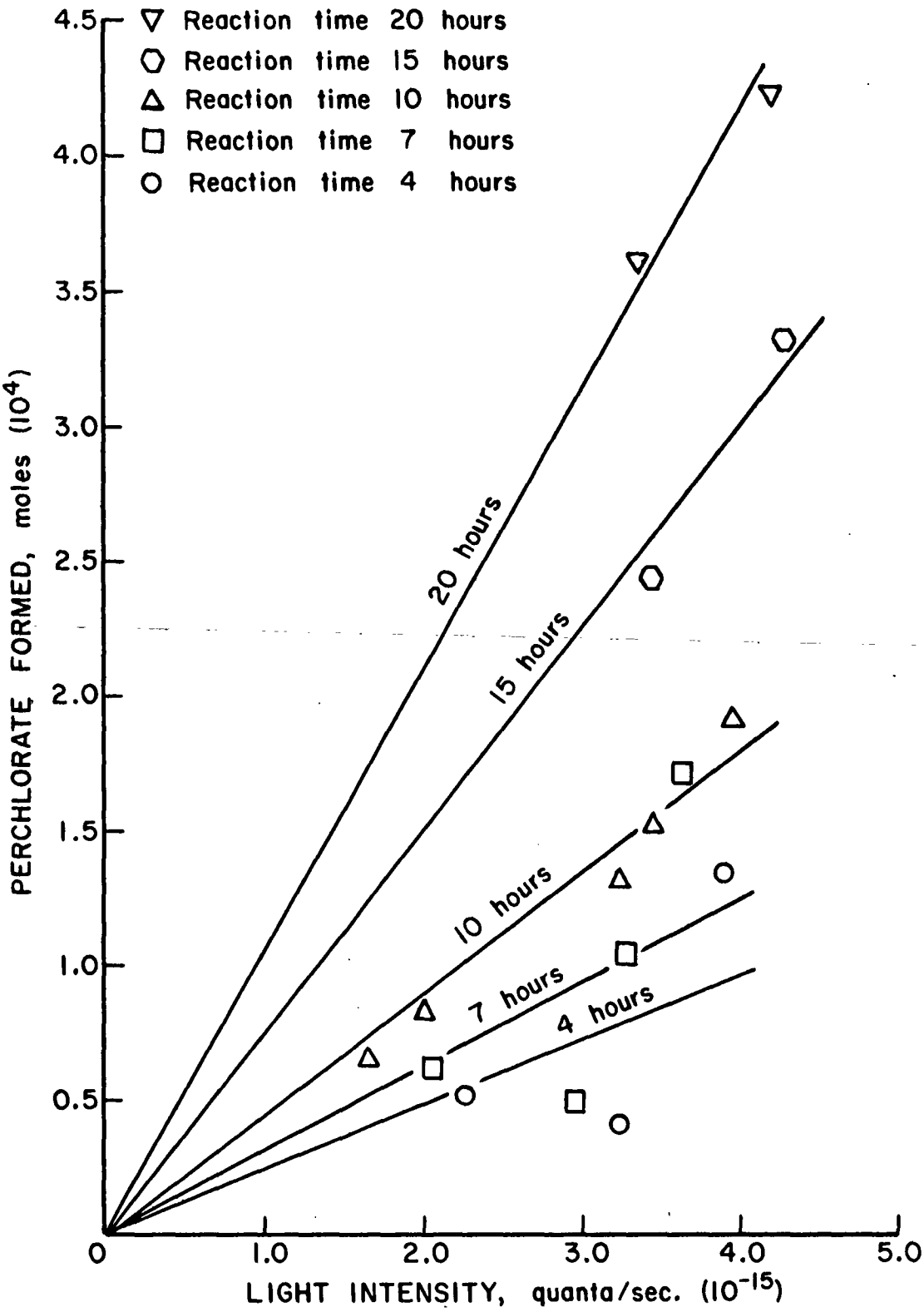


Figure 9. Moles of Perchlorate Formed vs. Light Intensity at Constant Time and Temperature of 0°C.

TABLE IX

EFFECT OF LIGHT INTENSITY ON PRODUCTION OF ClO_4^-, AT 0°C.
ADJUSTED TO THREE LEVELS OF LIGHT INTENSITY

Time of Run, hr.	Run	Light Intensity, quanta/sec. (10^{-15})	ClO_4^- Formed, moles (10^4)	Adjusted ClO_4^-, moles (10^4) Light Intensity Level, quanta/sec. (10^{-15})		
				2.00	3.05	4.00
4	20	2.27	0.52	0.45	--	--
	23	3.23	0.41	--	0.38	--
	49	3.89	1.34	--	--	1.38
7	21	2.05	0.62	0.60	--	--
	22	2.96	0.49	--	0.50	--
	27	3.28	1.04	--	0.96	--
	50	3.62	1.72	--	--	1.90
10	24	3.46	1.51	--	1.33	--
	28	3.23	1.31	--	1.24	--
	33	1.65	0.65	0.79	--	--
	36	1.99	0.83	0.83	--	--
	39	3.94	1.91	--	--	1.94
15	26	3.44	2.44	--	2.16	--
	47	4.27	3.32	--	--	3.11
20	25	3.33	3.61	--	3.31	--
	46	4.19	4.23	--	--	4.05
26	48	4.19	5.11	--	--	4.88

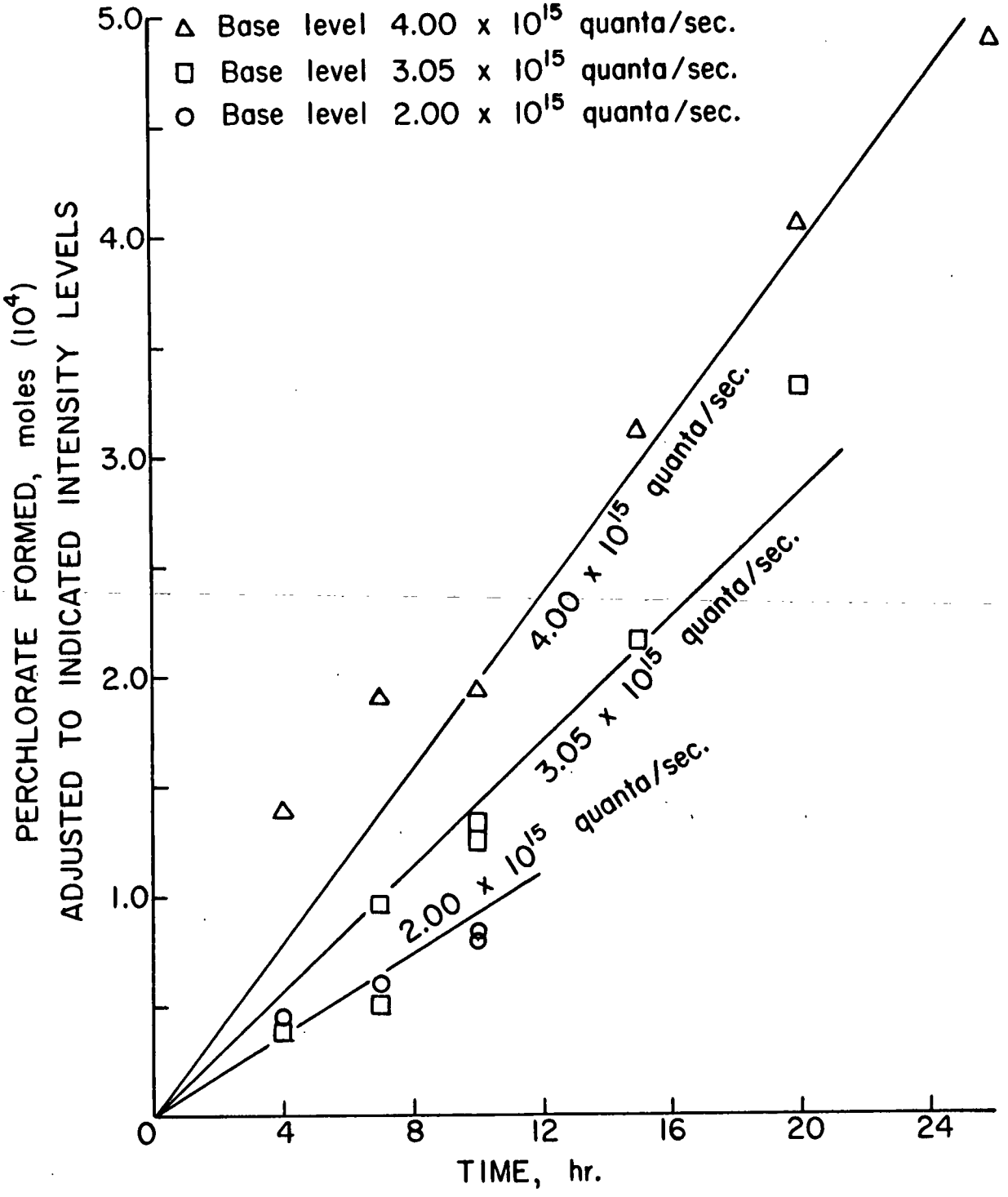


Figure 10. Adjusted Moles of Perchlorate Formed at Three Levels of Light Intensity vs. Time at 0°C.

Therefore, the product formed in the system under study could be formed in the primary process or in secondary reactions. However, due to the structural complexity of the product it is expected that it is formed in a secondary reaction.

TIME DEPENDENCE

As stated previously, experimental runs were made at two temperature levels (-10.5 and 0°C.) for a number of time periods. Table X presents the data obtained at -10.5°C. and Table XI the data obtained at 0°C., adjusted to a base light intensity of 3.05×10^{15} quanta/sec. (these data were previously given in Table VIII). Figures 11 and 12 plot adjusted moles of perchlorate formed versus the time of reaction for -10.5 and 0°C., respectively. For each plot, regression lines were prepared for the data between, and including, the four and twenty hour time intervals. For Fig. 11 the slope and intercept are 0.153 and 0.020, while for Fig. 12 they are 0.158 and -0.120.

Figures 11 and 12 allow the consideration of three areas of interest in the reaction sequence: induction period, constant rate period, and decline in rate. It is apparent from these figures that within the experimental error expected, both in the experimental and analytical procedures, the existence or nonexistence of an induction period cannot be proven. However, the presence of a constant rate period seems evident, and this constant rate is indicative of the overall rate of production of perchlorate at the respective temperature. Since data were not collected after a time interval of 26 hours, it cannot be shown conclusively that the break point of the constant rate period is at approximately 20 hours as was assumed when the regression analysis was made. However, qualitative evidence in the form of the reduction of the blue color of ozone in the carbon tetrachloride rinse material has shown that the

concentration of ozone has decreased. Therefore, it is evident that at some point the rate of production of perchlorate will decrease.

TABLE X

RESULTS OF EXPERIMENTAL RUNS AT -10.5°C., SAME REACTANT CONCENTRATION BUT VARIATION IN TIME

Time of Run, hr.	Run	Light Intensity, quanta/sec. (10^{-15})	ClO_4^- Formed, moles (10^4)	Adjusted ClO_4^-, moles (10^4)[b]
4	5	3.15	0.04	0.04
	7	2.83	0.75	0.81
	9	2.95	0.35	0.36
	12	3.04	1.31	1.31
	15[a]	2.41	0.81	1.02
	17	2.20	0.39	0.53
8	1	3.48	1.31	1.15
	2	3.65	1.53	1.28
14	8	3.09	2.50	2.47
	11	3.11	2.27	2.23
20	6	3.12	2.98	2.91
	10	3.06	3.03	3.01
26	13	2.76	3.20	3.53

[a] Not used because of reactor contamination.

[b] Moles of ClO_4^- adjusted to base light intensity of 3.05×10^{15} quanta/sec.

TABLE XI

RESULTS OF EXPERIMENTAL RUNS AT 0°C.,
SAME REACTANT CONCENTRATION BUT VARIATION IN TIME

Time of Run, hr.	Run	Light Intensity, quanta/sec. (10^{-15})	ClO_4^- Formed, moles (10^4)	Adjusted ClO_4^-, moles (10^4)[a]
4	20	2.27	0.52	0.69
	23	3.23	0.41	0.38
	49	3.89	1.34	1.05
7	21	2.05	0.62	0.92
	22	2.96	0.49	0.50
	27	3.28	1.04	0.96
	50	3.62	1.72	1.45
10	24	3.46	1.51	1.33
	28	3.23	1.31	1.24
	33	1.65	0.65	1.20
	36	1.99	0.83	1.28
	39	3.94	1.91	1.48
15	26	3.44	2.44	2.16
	47	4.27	3.32	2.37
20	25	3.33	3.61	3.31
	46	4.19	4.23	3.09
26	48	4.19	5.11	3.72

[a]Moles of ClO_4^- adjusted to base light intensity of 3.05×10^{15} quanta/sec.

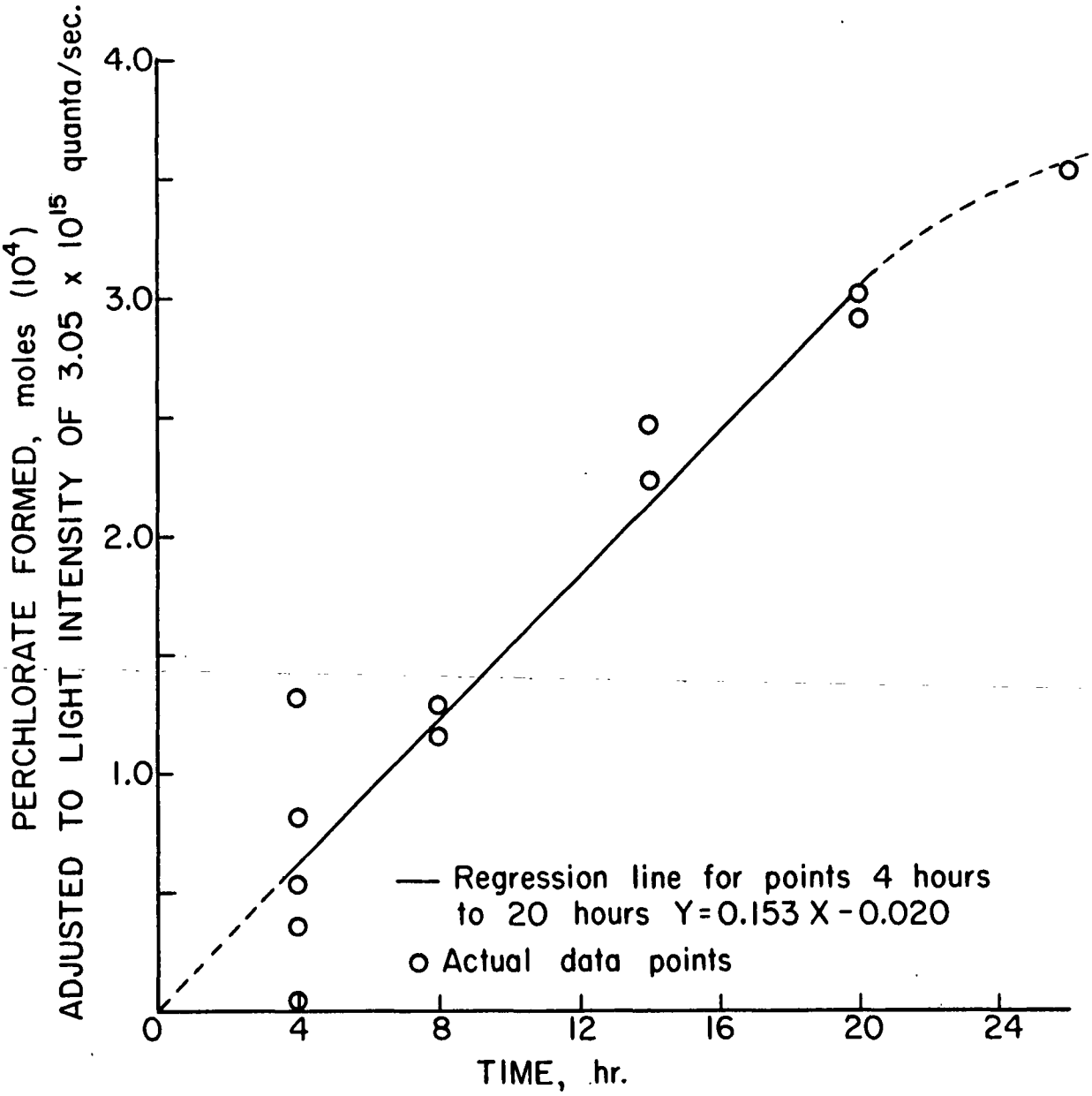


Figure 11. Adjusted Moles of Perchlorate Formed vs. Time at -10.5°C.

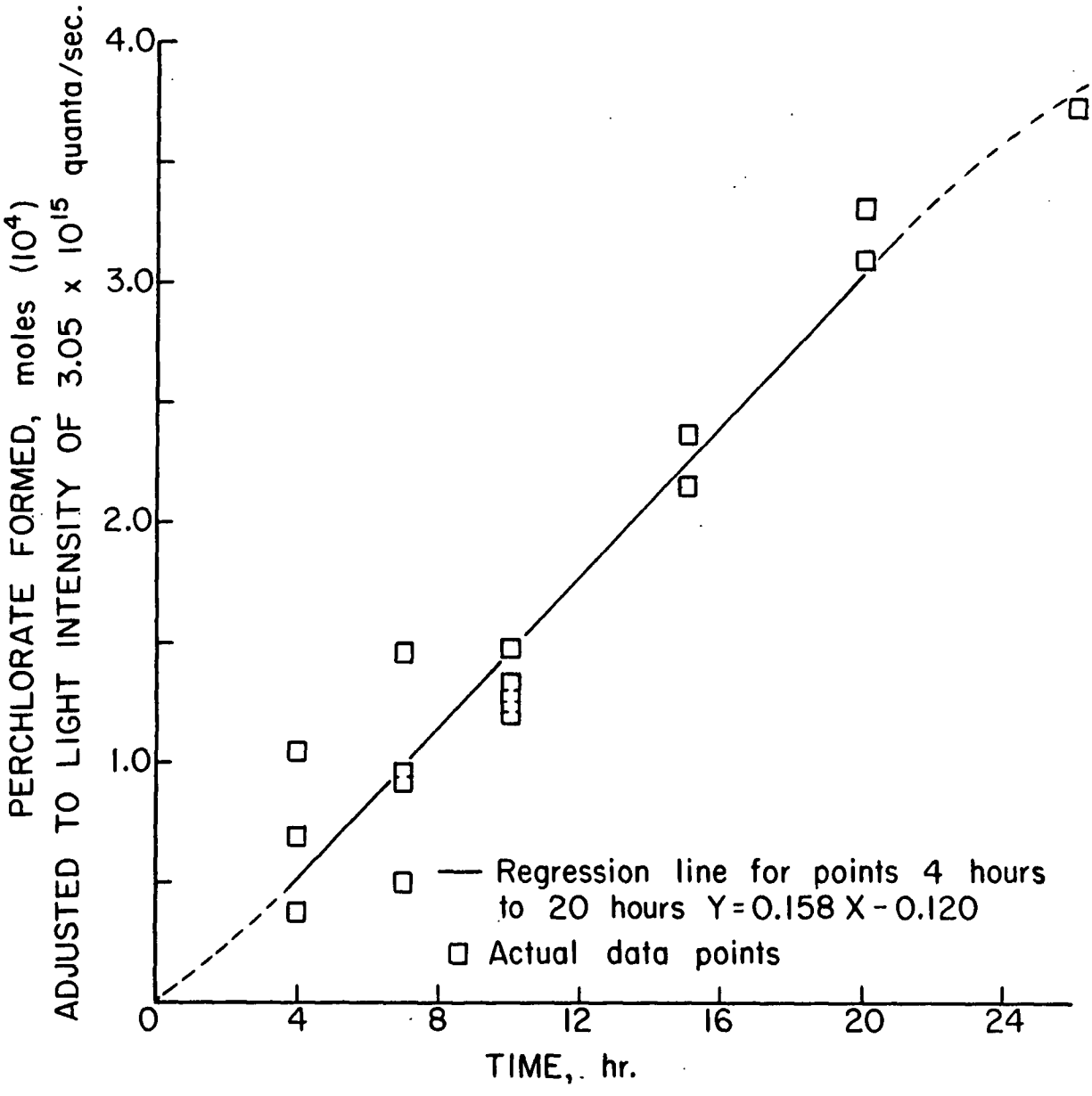


Figure 12. Adjusted Moles of Perchlorate Formed vs. Time at 0°C.

TEMPERATURE DEPENDENCE

Figure 13 presents the data plotted on Fig. 11 and 12 on the same axes. There is no significant difference between the two curves. Therefore, within the range of temperatures chosen for the study there is no temperature dependence. It is important to note that the temperatures chosen for the study were selected to minimize thermal degradation of the ozone and of the chlorine oxides formed. It is expected that temperatures above the levels used will cause a temperature dependence due to thermal degradation of ozone and chlorine oxides. Temperatures below the levels used may cause problems due to the vapor pressure of the reactants and products.

Calvert and Pitts (8) discuss the effect of temperature on the rate of photochemical reactions. In systems where there is no temperature dependence the product is usually formed in a primary process. However, there are some instances where a series of reactions are required to form the product but there is no temperature dependence. This can occur in two cases. The first case requires "hot" radicals. These are fragments of the original absorbing molecules which carry energy in excess of their normal thermal energy. They are very reactive since they carry the excess energy required to overcome the activation energy of resultant reactions. The second case occurs when the activation energies of the secondary reactions are very low. Therefore, the rate of formation of product is insensitive to temperature change.

As will be discussed later, the major chlorine oxide product found is dichlorine heptoxide. This leads to the formation of perchlorate in water. It is apparent that the formation of dichlorine heptoxide from ozone and chlorine must occur in some stepwise manner involving chlorine oxide intermediates. Therefore, it is expected that the excess energy of a "hot"

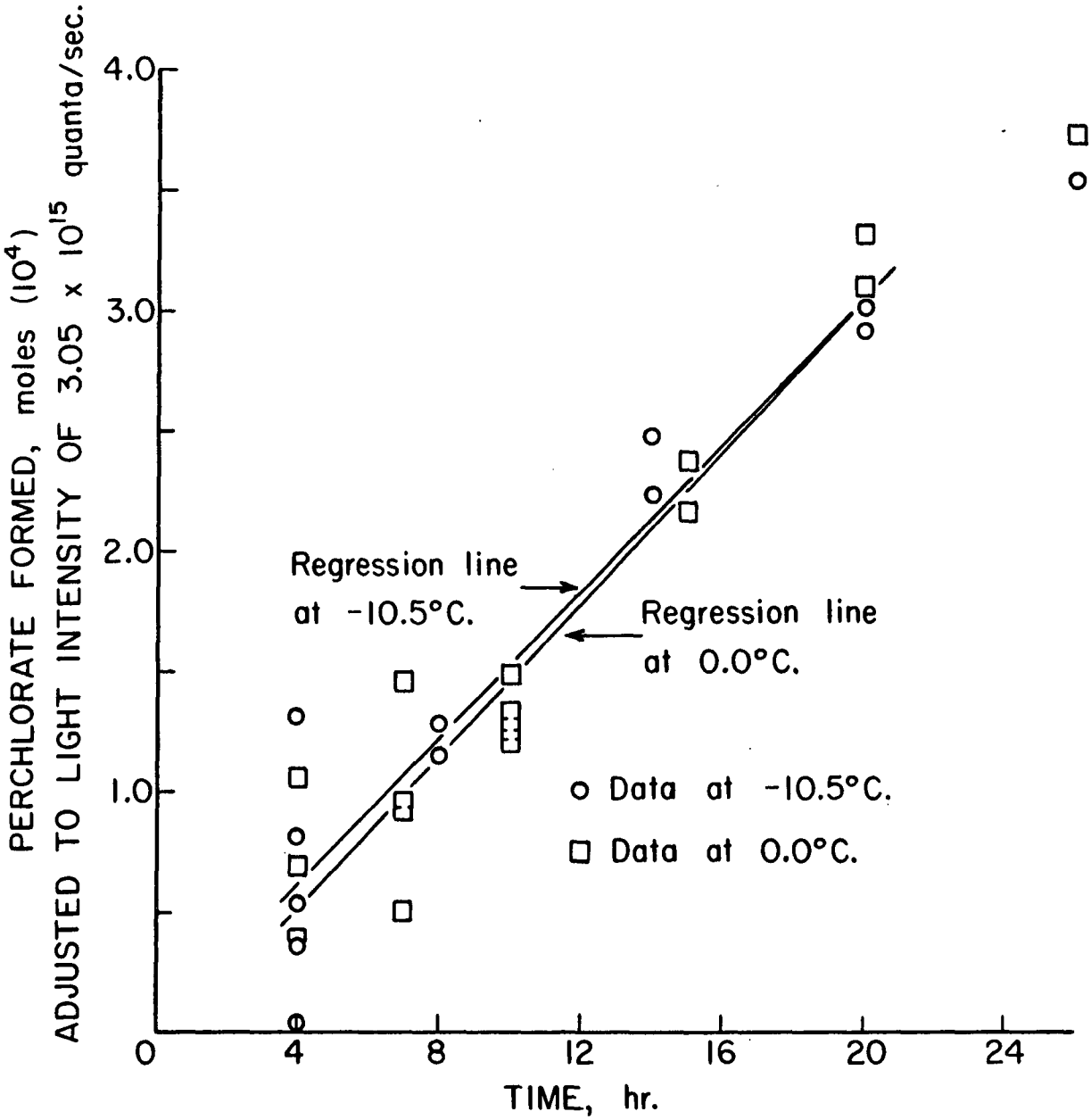


Figure 13. Adjusted Moles of Perchlorate Formed vs. Time at -10.5 and 0°C.

radical would not carry through to the production of the final product, although it may be necessary in an intermediate step. It is assumed, therefore, that the lack of temperature dependence is due to low activation energy reactions occurring in the stepwise process, with the possibility that a "hot" radical may initiate the chain.

THIRD BODY DEPENDENCE

It was of interest to determine the effect of diluents on the system. Therefore, instead of the usual practice of adding helium as a diluent, oxygen was used in place of helium in one series of reactions and no diluent was used in another series. The results of this work are given in Table XII. Since only two runs were made with oxygen and without helium, it was impossible to get reasonable 95% confidence limits for the averages. Therefore, the 95% confidence limits obtained for the five runs with helium were applied to these averages. A statistical analysis of the difference between the means showed that there was a significant difference between the means at the 80% confidence limit level. This trend indicates that under the conditions studied there is a slight drop in product production due to the introduction of a diluent gas. Oxygen appears to have a greater effect then helium.

Calvert and Pitts (8) discuss a number of effects that the addition of diluents will help to detect. First, the addition of a diluent should increase the rate of recombination of atoms and simple radicals, since these species usually require a third body for recombination. The rate of decomposition of some simple radicals may be increased due to increased collisions. Molecules containing higher than usual energy, "hot" radicals, would be deactivated faster due to more collisions. Reactions occurring at the wall of the vessel would be slowed because of lower diffusion rates of the reactants

to the wall. Since the trend in the present study is a decrease in product formation due to addition of diluent all of these effects might be occurring. Because the chlorine molecule in this system is dissociated to atoms and these atoms do recombine through a molecular collision, the first case is occurring. The presence of "hot" radicals has been mentioned in the previous section. The decomposition of simple radicals may occur. The possibility of diffusion controlled reactions cannot be eliminated because calculations given in Appendix XI show that the change in the diffusion coefficient of chlorine dioxide through the gaseous mixtures when the diluent is added is of the same order as the decrease in reaction due to introduction of He and oxygen. Chlorine dioxide was used in the calculations only because some required data were available not because it was assumed to be the necessary diffusing species.

TABLE XII

EFFECT OF He AND O_2 AS DILUENTS AND OF NO DILUENT AT 0°C. FOR 10-HOUR RUNS

Number of Runs	Moles Added (10^3)				Adjusted ClO_4^- Moles (10^4)[a]
	O_3	Cl_2	He	O_2	
2	5.39	5.38	--	--	1.46 ± 0.14
5	5.41	5.38	5.36	--	1.30 ± 0.14
2	5.40	5.38	--	5.45	1.21 ± 0.14

[a] Moles of ClO_4^- adjusted to base light intensity of 3.05×10^{15} quanta/sec.

OZONE DEPENDENCE

Table XIII presents the data obtained when the moles of ozone added were varied at a constant level of chlorine, $5.39 \pm 0.03 \times 10^{-3}$ moles, and varying He levels to give the same total pressure, 450 mm. Hg, in the 611.6-ml. reactor. Figure 14 is a plot of these data with moles of perchlorate versus moles of ozone added. It is obvious from the data that the production of product is related to the ozone level in a complex manner. It appears that at low ozone levels (less than 2.0×10^{-3} moles) there is a greater than zero order relationship with respect to ozone, but as the ozone level increases the relationship approaches a zero order one. There is further evidence for the approach to zero order. It has been shown that helium has a slight effect on the system. Since the total pressure of the system was obtained through addition of helium, runs at low ozone levels contain more helium and thus would be hindered to a greater extent. If the datum from Table XII where no He is added (1.46×10^{-4} moles perchlorate formed, at an ozone level of 5.39×10^{-3} moles) is plotted on Fig. 14, then this point and points obtained at higher ozone levels are almost horizontal indicating even a greater tendency for the approach to zero order.

This evidence explains why there is such a long constant rate period to the reaction despite qualitative evidence that ozone is being consumed. Since most reactions started at an ozone level of 5.40×10^{-3} moles, Fig. 14 indicates that even with a 50% decrease in ozone over the course of the reaction the final rate would remain so close to the original reaction rate that the change could not be detected.

TABLE XIII

EFFECT OF OZONE CONCENTRATION ON PERCHLORATE PRODUCTION FOR 10-HOUR RUNS AT 0°C.

Run	Light Intensity, quanta/sec. (10^{-15})	ClO_4^- Formed, moles (10^4)	Adjusted ClO_4^-, moles (10^4)[a]	O_3 at Start,[b] moles (10^3)
29	3.46	1.59	1.40	3.32
44	4.43	1.76	1.21	3.59
24	3.46	1.51	1.33	5.39
28	3.23	1.31	1.24	5.43
33	1.65	0.65	1.20	5.47
36	1.99	0.83	1.27	5.40
39	3.94	1.91	1.48	5.42
34	1.91	0.78	1.25	7.44
45	4.39	2.12	1.48	8.99
30	3.38	1.65	1.49	10.50
37	1.96	0.68	1.05	10.78
35	2.16	1.12	1.58	10.79

[a] Moles of ClO_4^- adjusted to base light intensity of 3.05×10^{15} quanta/sec.
[b] At a constant chlorine level of $5.39 \pm 0.03 \times 10^{-3}$ moles.

TOTAL PRESSURE RISE IN THE SYSTEM

Throughout the experimental program the pressure rise in the reactor during experimental runs has been small. The increase in moles of gas in the system has been calculated from this pressure rise and compared to the moles of perchlorate formed. It will be shown later that one-half the number of moles of perchlorate formed is equal to the number of moles of dichlorine heptoxide formed. These data are presented in Table XIV for reactions run at

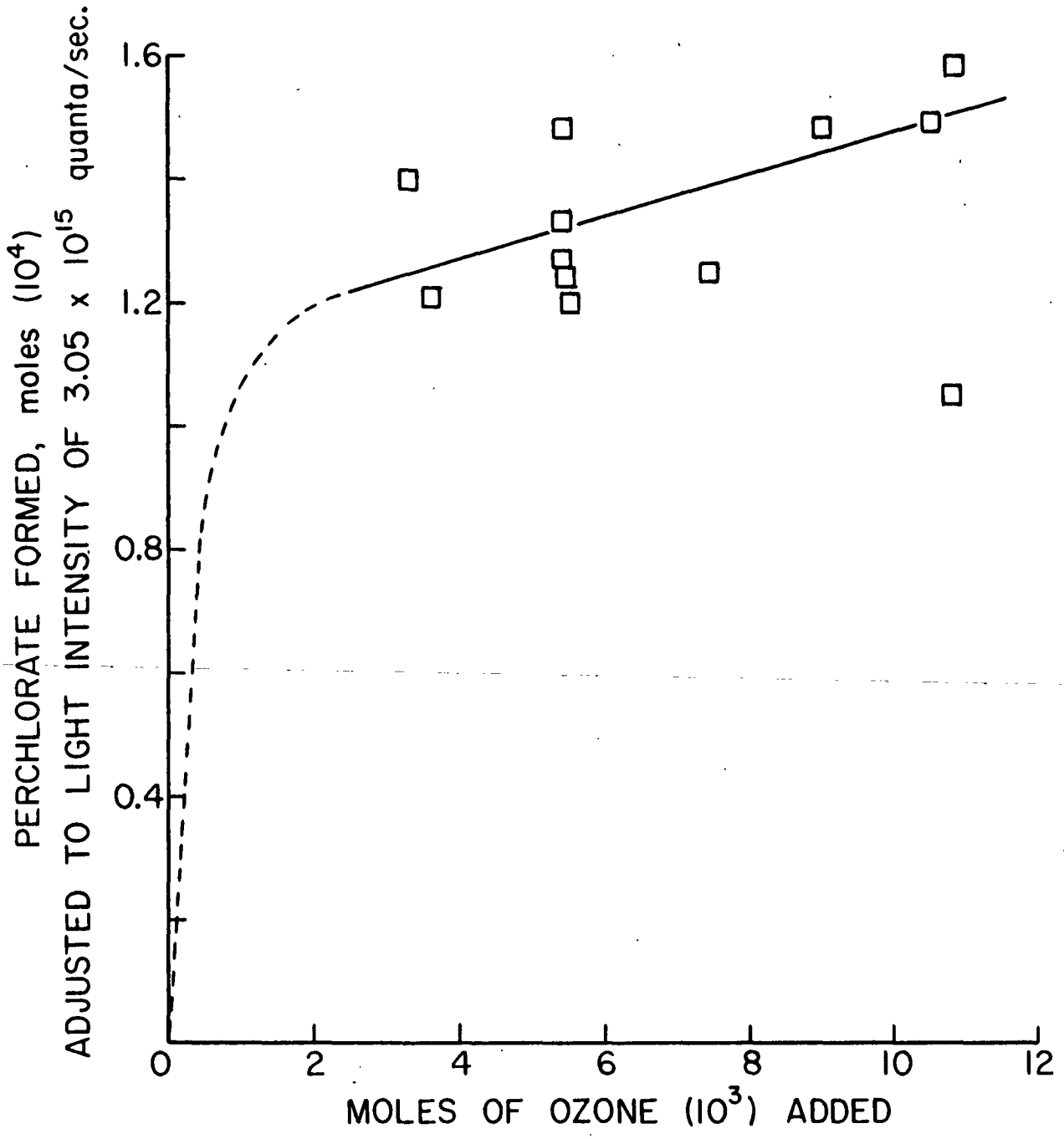


Figure 14. Adjusted Moles of Perchlorate Formed vs. Moles of O_3 Added for 10 Hour Runs at 0°C.

0°C. using helium as the diluent. It is seen that the increase in moles in the system, except for one case, is equal to or less than the number of moles of dichlorine heptoxide formed. Since ozone is the only reactant that can decompose, it is assumed that decomposition of ozone to oxygen accounts for the increase in total moles in the system. Since the formation of high chlorine oxides, chlorine trioxide, dichlorine hexoxide, and dichlorine heptoxide, would represent a net decrease in total moles, there must be a balancing of moles between chlorine oxide formed and ozone destroyed to form oxygen. Possibly the reactions leading to the formation of chlorine oxides result in no net change in total moles, while the increase in total moles in the system is due to unproductive side reactions that decompose ozone.

TABLE XIV

PRESSURE AND CONCENTRATION CHANGES IN THE REACTOR DURING DIFFERENT REACTION TIMES AT 0°C. AND THE SAME REACTANT CONCENTRATIONS

Time of reaction, hr.	4	7	10	15	20	26
Change in pressure, mm. Hg	-0.67	0.40	1.76	1.90	6.75	5.20
Change in total moles (10^4)	-0.24	0.14	0.63	0.68	2.42	1.87
Adjusted ClO_4^-, moles (10^4)[a]	0.71	0.96	1.30	2.27	3.20	3.72
Cl_2O_7 formed, moles (10^4)	0.35	0.48	0.65	1.14	1.60	1.86

[a]Moles of ClO_4^- adjusted to base light intensity of 3.05×10^{15} quanta/sec.

One characteristic of the total pressure in the system is indicated by the change in pressure (-0.67 mm. Hg) given for the four-hour runs in Table XIV. All runs gave a characteristic decrease in total pressure followed by a gradual increase. This decrease was not more than 1 mm. of Hg. Three explanations can be given for this phenomenon: products being formed are preferentially absorbed

onto the surface of the reactor vessel; products are reacting with a substance on the walls; and, the reactant gases have not come to thermal equilibrium after introduction. The third possibility is discounted because the pressure decrease occurred over a period of several hours. Possibilities one and two could occur but explanation two was chosen because evidence was found of a film forming in the reactor which appeared to have its greatest density on those portions of the reactor closest to where the light beam enters. This film was not soluble in carbon tetrachloride. If the film consisted of dichlorine hexoxide or dichlorine heptoxide it would be soluble in carbon tetrachloride. The film was soluble in water. Therefore, it is felt that initial products of the reaction, upon striking the wall of the vessel, reacted with water absorbed on the wall and were held on the wall as ionic species which were not removed by carbon tetrachloride. This film was probably similar to that reported by Allmand and Spinks (36) when slightly wet gases were used. In the present system it was due to water on the walls which could not be removed by simply pulling a vacuum on the system.

QUANTUM YIELD

The quantum yield of a photochemical reaction is a measure of the efficiency of the reaction. It is the ratio of the number of molecules of a species formed divided by the number of quanta absorbed. Several types of quantum yields are used in photochemistry: primary quantum yields (related to the primary absorption process), product quantum yields (based on the amount of a final product formed), and others based on fluorescence, decomposition, rearrangement, etc. The two types of quantum yield considered in this work are primary and product quantum yields, ϕ. The primary quantum yield considered in this study is the number of chlorine atoms formed per quantum of

energy absorbed. Therefore, according to Equation (17) found on page 227 of Calvert and Pitts (8),

$$Cl_2(^1\Sigma_g^+) + h\nu \longrightarrow Cl_2(^3\pi_{o+u}) \longrightarrow Cl(^2P_{3/2}) + Cl(^2P_{1/2}), \qquad (17)$$

the primary quantum yield in the system is 2. The product quantum yield, ϕ, is based on the number of molecules of perchlorate formed during the reaction. Therefore, theoretically, if each atom of chlorine produced a molecule of perchlorate the ϕ would be 2. Table XV presents the results of calculations for ϕ for data obtained at -10.5°C. and 0°C. At each temperature the starting conditions were similar. The moles of perchlorate produced at each reaction time is an average of several experimental runs. The 26.0-hour runs are individual points. These data again point out the lack of temperature dependence in the system as the common average of the ϕ at each temperature attests. The data also show that the ϕ is less than the theoretical; therefore, certain inefficiencies are entering into the reaction.

TABLE XV

PRODUCT QUANTUM YIELD AT -10.5°C. AND 0°C.

Temperature, °C.	Time of Reaction, hr.	Adjusted ClO_4^-, moles (10^4)[a]		Product Quantum Yield, ϕ
-10.5	4.0	0.61		0.84
	8.0	1.21		0.83
	14.0	2.35		0.92
	20.0	2.96		0.81
	26.0	3.53		0.74
			Average	0.83
0.0	4.0	0.71		0.97
	7.0	0.96		0.75
	10.0	1.30		0.71
	15.0	2.27		0.83
	20.0	3.20		0.88
	26.0	3.72		0.79
			Average	0.82

[a]Moles of ClO_4^- adjusted to base light intensity of 3.05×10^{15} quanta/sec.

Calvert and Pitts (8) discuss the mechanisms of photochemical reactions in relation to their quantum yields. In a case where the theoretical quantum yield is two when ϕ is much less than two ($\phi << 2$), it is an indication of major processes within the reaction that lead to no net chemical change. When ϕ is much larger than two ($\phi >> 2$), it is an indication of a chain reaction. When ϕ is near two it is an indication of the product being formed in a primary process or in a nonchain step. As suggested previously, the formation of product is expected to be a stepwise process because of its structural complexity. The fact that ϕ is less than the theoretical two for this system indicates that some reactions are occurring that involve the absorption of quanta but do not lead to a final product. In a later section the nature of these reactions will be discussed.

INTERPRETATION OF REACTION PARAMETERS

An interpretation of the preceding presentation allows a consolidation of the ideas presented and elimination of certain possibilities regarding a reaction mechanism. The data indicate a direct relationship between light intensity and product formation.

Since there is no temperature dependence, the product must be formed in the primary process or in a secondary process involving low activation energies or "hot" radicals. Because of the structural complexity of the final product, the formation of the product in the primary process is not possible. Therefore, the product is formed in a stepwise secondary process either through low activation energy reactions or "hot" radicals.

The slight decrease in product formation due to introduction of helium and oxygen as diluents can be explained by four different possibilities: atom

recombination, decomposition of simple radicals, deactivation of "hot" radicals, and lowered diffusion rates slowing reactions occurring at the wall. None of these possibilities can be eliminated. Oxygen appears slightly more efficient than helium in decreasing product formation.

The product relationship with ozone concentration indicates a greater than zero order reaction with respect to ozone followed by an approach to zero order. This seems to be substantiated by the long constant rate portion of the rate curve despite qualitative evidence that the ozone concentration is decreasing.

Little or no induction period indicates that there is little time delay in building up the concentration of necessary intermediates for the stepwise formation of product.

Little pressure rise in the system indicates that products are formed to reduce the total moles in the system at about the same rate as oxygen is produced to increase the moles in the system.

The product quantum yield indicates that reactions are occurring which do not lead to product formation. Therefore, side reactions may be occurring which recombine chlorine atoms and produce oxygen from ozone to give the slight pressure increase encountered. The product quantum yield also indicates that the stepwise formation of product is not a chain reaction.

DEVELOPMENT OF A REACTION MECHANISM

The following section will develop a mechanism which is consistent with the data obtained and with that already available about the system. First, the data obtained will be discussed with respect to which chlorine oxides produced the perchlorate product. The mechanism is then developed with special

emphasis on the primary process, product forming secondary reactions, and side reactions. Finally, the mechanism is evaluated with respect to unimportant side reactions, known facts, and estimated information about the system.

CHLORINE OXIDE PRODUCTS

As discussed in the section "Parameters of the Reaction," the major product found was perchlorate ion. The perchlorate formed is a result of chlorine oxide products reacting with the water during and after removal from the reactor. The only chlorine oxides that react with water to form perchlorate are dichlorine hexoxide and dichlorine heptoxide (4). However, dichlorine hexoxide also forms equal quantities of chlorate ion. As mentioned previously, no chlorate ion has been found in substantial quantities in conjunction with perchlorate ion; therefore, the presence of dichlorine hexoxide is negligible, though its presence in the reaction system is not ruled out. Dichlorine heptoxide is considered to be the major product of the reaction. When placed in water, one molecule of dichlorine heptoxide forms two ions of perchlorate,

$$Cl_2O_7 + H_2O \longrightarrow 2\ H^+ + 2\ ClO_4^-. \qquad (93)$$

Therefore, if the preceding figures and tables are to be considered in terms of dichlorine heptoxide, the moles of product in terms of perchlorate must be divided by two to get moles of product as dichlorine heptoxide. For example, Table XVI presents the data of Table XII converted to dichlorine heptoxide. The mechanism presented will be in terms of the gaseous reaction product, dichlorine heptoxide. Since there is a direct proportion between perchlorate and dichlorine heptoxide, the conclusions reached concerning the formation of perchlorate will also hold for dichlorine heptoxide. The presence of other

chlorine oxides are also indicated in the proposed mechanism. However, they are thought to exist in the reaction system at concentrations below a detectable level.

TABLE XVI

AVERAGE RATE OF FORMATION AND QUANTUM YIELD OF FORMATION OF Cl_2O_7 AT 0°C. FOR 10-HOUR RUNS

Diluent	Adjusted ClO_4^-, moles (10^4)[a]	Cl_2O_7, moles (10^4)	Rate of Formation of Cl_2O_7[b], moles/liter sec. (10^8)	Quantum Yield of Formation of Cl_2O_7
None	1.46 ± 0.14	0.73 ± 0.07	1.31 ± 0.13	0.401
He	1.30 ± 0.14	0.65 ± 0.07	1.16 ± 0.13	0.356
O_2	1.21 ± 0.14	0.61 ± 0.07	1.09 ± 0.13	0.332

[a] Moles of ClO_4^- adjusted to base light intensity of 3.05×10^{15} quanta/sec.
[b] Rate based on reaction zone, 0.155 liter.

THE MECHANISM

The mechanism as presented here consists of a primary process and secondary thermal processes. The secondary thermal processes include product forming secondary reactions, and side reactions. Each group of reactions will be considered as a separate part. Elimination of unimportant side reactions and manipulation of the mechanism to get important rate functions will be left to the next section.

The Primary Process

The primary process in this system is the absorption of a quantum of energy by chlorine and the subsequent dissociation of chlorine into chlorine atoms.

$$Cl_2(^1\Sigma^+_g) + h\nu \longrightarrow Cl_2(^3\pi_{o+u}) \longrightarrow Cl(^2P_{3/2}) + Cl(^2P_{1/2}) \qquad (17)$$

This reaction and two side reactions are the only reactions involving the absorption of light. Equation (17) can be described in words as absorption by a ground state chlorine molecule, $Cl_2(^1\Sigma^+_g)$, of a quantum of light of wavelength 365-366.5 nm. to form an excited state, $Cl_2(^3\pi_{o+u})$, which dissociates on its first vibration to one ground state, $Cl(^2P_{3/2})$, and one excited, $Cl(^2P_{1/2})$, chlorine atom. Since in this system there is no way to distinguish between ground state and excited chlorine atoms, and because the frequency separation between the $^2P_{3/2}$ and $^2P_{1/2}$ chlorine atoms is only 881 $cm.^{-1}$ (2.52 kcal./mole), they will be treated alike and represented in equations with the symbol Cl. It is doubtful that the slight increase in energy of the $^2P_{1/2}$ chlorine atom will make it significantly more reactive in the system.

Product Forming Secondary Reactions

As indicated previously the final product formed in this system is dichlorine heptoxide. The data indicate that it is produced in a nonchain stepwise procedure, which causes little or no increase in the final pressure of the system. The series of reactions that produce dichlorine heptoxide either have to involve "hot" radicals or have low activation energies in order to have no temperature dependence. The reactions in the stepwise procedure will be considered to have low activation energies. Since it has been shown by Johnston, et al. (35) that ClO, ClOO, and dichlorine dioxide (Cl_2O_2) are the only chlorine oxide species formed during the photolysis of chlorine in oxygen, ozone must be the active species that leads to the formation of higher chlorine oxides, chlorine dioxide, chlorine trioxide, and dichlorine heptoxide. The photolysis of chlorine in oxygen is essentially the recombination of chlorine atoms due to

oxygen. Johnston, et al. have also shown that the concentration of ClO, ClOO, and dichlorine dioxide is increased by the addition of more oxygen to the system while the chlorine atom concentration is decreased. In the system under study there was a slight decrease in product formation when oxygen was added. This indicates that ClO, ClOO, and dichlorine dioxide are probably not intermediates in the stepwise formation of dichlorine heptoxide because if they were one would expect an increase in the formation of dichlorine heptoxide because of the increase in their concentration. The addition of oxygen and the resultant decrease in chlorine atom concentration appears to be the reason for the drop in dichlorine heptoxide formation.

The proposed first step in the reaction mechanism for formation of dichlorine heptoxide and decomposition of ozone is the reaction between chlorine atoms and ozone to form a chlorine-ozone activated complex ($ClOOO^*$),

$$Cl + O_3 \longrightarrow ClOOO^*. \qquad (94)$$

This complex is unstable and either decomposes to ClO and oxygen or is struck by a third body which carries off excess energy to render it slightly more stable.

$$ClOOO^* \longrightarrow ClO + O_2 \qquad (95)$$

$$ClOOO^* + M \longrightarrow ClOOO + M. \qquad (96)$$

Equations (94), (95), and (96) can be rewritten as follows:

$$Cl + O_3 + M \longrightarrow ClOOO + M \qquad (97)$$

$$Cl + O_3 \longrightarrow ClO + O_2. \qquad (39)$$

Equations (97) and (39) are the key to the explanation of the mechanism. Equation (97) predominates under conditions of increased chlorine and oxygen concentrations. This leads to production of dichlorine heptoxide and

decomposition of ozone which is proportional to the absorbed light intensity. Equation (39) predominates at conditions of low chlorine and oxygen concentrations where ozone decomposition is proportional to the light intensity absorbed to the 0.5 power. The third body in Equation (97) is considered to be any available third body, ozone, oxygen, chlorine, and helium, in the experimental system. Each one of these species is expected to have different efficiencies of stabilization of the ClOOO complex. Equation (97) is similar to the known reaction,

$$Cl + O_2 + M \longrightarrow ClOO + M. \qquad (77)$$

The second proposed reaction in the stepwise sequence is shown by Equation (98),

$$ClOOO + O_3 \longrightarrow ClO_2 + 2\,O_2. \qquad (98)$$

Here the ClOOO complex reacts with ozone to form chlorine dioxide and two molecules of oxygen. It is possible that chlorine dioxide may be formed directly if M in Equation (97) is ozone which for high ozone concentrations would be quite frequent. Equation (98) may be replaced by Equation (50),

$$ClO + O_3 \longrightarrow ClO_2 + O_2, \qquad (50)$$

but ClO, as already discussed, must have a small effect on the formation of dichlorine heptoxide. It will be shown later in discussion on the evaluation of the mechanism that the concentration of ClO is greater in those systems that originally contain oxygen and accounts for increased decomposition of ozone through Equation (40),

$$ClO + O_3 \longrightarrow Cl + 2\,O_2. \qquad (40)$$

Equation (40) is favored over Equation (50) since ΔG°_{298} for Equation (40) is -37.19 kcal./mole and ΔG°_{298} for Equation (50) is -33.06 kcal./mole. The calculations for ΔG°_{298} were based on data obtained from the JANAF Thermochemical Tables (55).

The third reaction in the stepwise sequence is shown by Equation (10),

$$ClO_2 + O_3 \longrightarrow ClO_3 + O_2. \qquad (10)$$

This reaction is well established in work with chlorine oxides. The production of dichlorine hexoxide, the liquid dimer of gaseous chlorine trioxide, has been accomplished in the laboratory using this basic reaction (68). Two streams of gas, one containing ozone and one chlorine dioxide, are mixed in a vessel and then passed through a gas trap at a temperature of 0°C. to condense the chlorine trioxide formed to dichlorine hexoxide. It is a very fast reaction and meets the criterion set up for product forming secondary reactions.

The last reaction of the product forming secondary reactions is given by Equation (51),

$$2\ ClO_3 + O_3 \longrightarrow Cl_2O_7 + O_2. \qquad (51)$$

Equation (51), as are Equations (97) and (98), is purely speculative but it has been suggested by Goodeve and Marsh (50). It is envisioned that a collision between ozone and chlorine trioxide can form a rather long-lived complex which could be stabilized by the collision energy being distributed among its numerous bonds. Upon collision with a molecule of chlorine trioxide this complex reacts to form dichlorine heptoxide and oxygen.

Equation (51) could be replaced by reactions suggested by other workers,

$$ClO_3 + O_3 \longrightarrow ClO_4 + O_2 \qquad (31)$$

$$ClO_3 + ClO_4 \longrightarrow Cl_2O_7 \qquad (32)$$

$$2\ ClO_3 \longrightarrow ClO_2 + ClO_4 \qquad (34)$$

$$ClO_3 + ClO_4 \longrightarrow Cl_2O_7 \qquad (32)$$

$$Cl_2O_6 + O \longrightarrow Cl_2O_7. \qquad (63)$$

Equations (31) and (32) are essentially those suggested by Rollefson and Byrns (42). Equations (34) and (32) have been suggested by Schumacher (56) and Arvia, et al. (46). Equation (63) has been suggested by Spinks and Taube (63, 64). Equations (31) and (32) seem very plausible and there is very little difference between them and Equation (51). Equation (51) has been favored because the existence of chlorine tetroxide seems somewhat doubtful and because if chlorine tetroxide does exist it is a very short-lived radical and thus the potential for its collision with a molecule of chlorine trioxide is very small. The sequence of Equations (34) and (32) seems doubtful because there is no reported evidence for the formation of dichlorine heptoxide during thermal decomposition of chlorine trioxide. Although Equation (63) may occur in the system of Spinks and Taube, it probably does not occur in the system under study because of the absence of dichlorine hexoxide and, as will be shown later, oxygen atoms. Therefore, Equation (51) appears more plausible for the formation of dichlorine heptoxide.

As was discussed earlier, when chlorine and oxygen concentrations are low, the ozone decomposition becomes a chain mechanism. The chain is believed started by Equation (39) and the cyclic process continued by Equation (40) as suggested by Norrish and Neville (49),

$$ClO + O_3 \longrightarrow Cl + 2\ O_2. \qquad (40)$$

Therefore, ClO is considered the chain carrier.

The proposed sequence of reactions leading to the formation of dichlorine heptoxide and decomposition of ozone becomes:

$$Cl_2(^1\Sigma_{g^+}) + h\nu \longrightarrow Cl_2(^3\pi_{o+u}) \longrightarrow Cl(^2P_{3/2}) + Cl(^2P_{1/2}) \qquad (17)$$

$$Cl + O_3 + M \longrightarrow ClOOO + M \qquad (97)$$

$$ClOOO + O_3 \longrightarrow ClO_2 + 2\,O_2 \qquad (98)$$

$$ClO_2 + O_3 \longrightarrow ClO_3 + O_2 \qquad (10)$$

$$2\,ClO_3 + O_3 \longrightarrow Cl_2O_7 + O_2 \qquad (51)$$

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (39)$$

$$ClO + O_3 \longrightarrow Cl + 2\,O_2. \qquad (40)$$

It can be seen that this sequence meets many of the criteria set up for the production of dichlorine heptoxide from chlorine and ozone by photoexcitation of chlorine, as studied in the present work, and for the decomposition of ozone, as presented in the "Literature Review": (1) dichlorine heptoxide is formed in a nonchain stepwise procedure; (2) the reactions are considered to have low activation energies, thus there is no temperature dependence; (3) there is no net increase or decrease of total moles in the system due to production of dichlorine heptoxide since one molecule of chlorine and seven molecules of ozone produce one molecule of dichlorine heptoxide and seven molecules of oxygen; (4) an increase in pressure in the system can be accounted for through Equation (40) which decomposes ozone without formation of dichlorine heptoxide or intermediates; (5) ozone is also decomposed through Equation (39) without formation of dichlorine heptoxide or an intermediate but does not result in an increase in pressure (6) in the formation of dichlorine heptoxide a direct relationship with light intensity is implied because the higher the light intensity the higher the chlorine atom concentration; (7) because of almost instantaneous attainment of chlorine atom concentration and the high concentration of ozone, it appears

that equilibrium concentrations of ClOOO, chlorine dioxide, and chlorine trioxide will be built up very fast so that little or no induction period is evident; and (8) furthermore, if Equations (17), (97), (98), (10), and (51) are considered and if the steady-state assumption for chlorine atom, ClOOO, chlorine dioxide, and chlorine trioxide is employed, the rate of production of dichlorine heptoxide becomes directly proportional to light intensity with a zero-order relationship with respect to ozone.

Equations (39) and (40) account for the chain decomposition of ozone that has been reported but do not account for the approach to an $I_{abs}^{0.5}$ relationship for the rate of destruction of ozone. Other experimental evidence not accounted for by the sequence are: (1) reduction of quantum yield of dichlorine heptoxide from a theoretical 1, and (2) an ozone relationship with dichlorine heptoxide formation which starts out greater than zero order and then approaches zero order with increasing ozone concentration. These effects are considered to be caused by reactions in the system which do not lead directly to formation of dichlorine heptoxide or chain decomposition of ozone. These reactions are termed side reactions.

Side Reactions

The side reactions occurring in this system are numerous and they are expected to cause the deviations expressed above. Johnston, et al. (35) have studied the photolysis of chlorine in oxygen. This system contains eight reactions which account for chlorine and oxygen interactions. Since oxygen is an inherent part of the system under study, the reactions studied by Johnston, et al. must be considered side reactions.

$$Cl + O_2 + M \longrightarrow ClOO + M \quad (77)$$

$$ClOO + M \longrightarrow Cl + O_2 + M \quad (78)$$

$$Cl + ClOO \longrightarrow ClO + ClO \quad (79)$$

$$ClO + ClO \longrightarrow Cl + ClOO \quad (80)$$

$$Cl + ClOO \longrightarrow Cl_2 + O_2 \quad (81)$$

$$ClO + ClO + M \longrightarrow Cl_2O_2 + M \quad (82)$$

$$Cl_2O_2 + M \longrightarrow ClO + ClO + M \quad (83)$$

$$Cl_2O_2 + M \longrightarrow Cl_2 + O_2 + M. \quad (84)$$

Additional side reactions are those involving interactions of the proposed intermediates and reactants. Since interactions of ClO, ClOO, and dichlorine dioxide have already been presented, the discussion will start with possible side reactions of chlorine dioxide. Chlorine dioxide could react with chlorine, oxygen, ClOO, dichlorine dioxide, chlorine dioxide, ClOOO, chlorine trioxide, and dichlorine heptoxide. The direct reaction of chlorine dioxide with chlorine and oxygen has never been observed. The reaction of chlorine dioxide with ClOO, dichlorine dioxide, ClOOO, chlorine trioxide, and itself seems remote because of the small concentration of these species ($<1.0 \times 10^{-8}$ moles/liter). The reaction of chlorine dioxide with dichlorine heptoxide also seems remote since dichlorine heptoxide is the most stable of the chlorine oxides. Four reported reactions of chlorine dioxide should be present in this system.

$$ClO_2 + Cl \longrightarrow 2\ ClO \quad (37)$$

$$ClO_2 + h\nu \longrightarrow ClO + O \quad (59)$$

$$ClO_2 + O \longrightarrow ClO + O_2 \quad (75)$$

$$ClO_2 + O + M \longrightarrow ClO_3 + M. \quad (60)$$

Equation (37) was used by Clyne and White (47) to produce ClO so that its decomposition rate could be studied. Equation (59) is the initial reaction in

the photochemical decomposition of chlorine dioxide at a wavelength of 365-366.5 nm. Equation (75) is discussed by Clyne and Coxon (67). Equation (60) has been suggested by Spinks and Porter (62) as the way chlorine trioxide is formed in photolysis of chlorine dioxide.

Side reactions involving chlorine trioxide could occur with chlorine, oxygen atom, oxygen, ClO, ClOO, dichlorine dioxide, ClOOO, and dichlorine heptoxide. The direct reaction of chlorine trioxide with chlorine and oxygen has never been observed and reaction of chlorine trioxide with dichlorine heptoxide seems doubtful because of the stability of dichlorine heptoxide. Reaction of chlorine trioxide with oxygen atom, ClO, ClOO, dichlorine dioxide, and ClOOO is possible but due to their low concentrations probably is negligible. Five reported reactions of chlorine trioxide could occur in the system.

$$2\ ClO_3 \longrightarrow 2\ ClO_2 + O_2 \qquad (33)$$

$$ClO_3 + Cl \longrightarrow ClO_2 + ClO \qquad (38)$$

$$ClO_3 + O_3 \longrightarrow ClO_2 + 2\ O_2 \qquad (11)$$

$$ClO_3 + h\nu \longrightarrow ClO_2 + O \qquad (76)$$

$$2\ ClO_3 \longrightarrow Cl_2O_6. \qquad (13)$$

Equations (33), (38), and (11) are suggested by Byrns (41). Equation (76) is the proposed reaction for decomposition of chlorine trioxide by light of wavelength 365-366.5 nm. Equation (13) is merely the condensation of chlorine trioxide to dichlorine hexoxide.

The reaction of dichlorine heptoxide with any of the species considered above seems doubtful. Thermal degradation of dichlorine heptoxide is limited by the temperature. Other possible reactions in the system could be:

$$ClO + O \longrightarrow Cl + O_2 \qquad (99)$$

$$Cl_2 + O \longrightarrow ClO + Cl \qquad (56)$$

$$2\ Cl + Cl_2 \longrightarrow 2\ Cl_2 \qquad (100)$$

$$2\ Cl + He \longrightarrow Cl_2 + He \qquad (101)$$

$$Cl \xrightarrow{\text{wall}} 1/2\ Cl_2 . \qquad (74)$$

Equations (99) and (56) are discussed by Niki and Weinstock (51). Equations (100) and (101) are the recombination of chlorine atoms by the third bodies, chlorine and He. Equation (74) is the recombination of chlorine atoms at the wall of the vessel.

The following section will discuss the mechanism in terms of which side reactions are significant and will present a simplified version of the mechanism which will allow attainment of rate equations for formation of dichlorine heptoxide and decomposition of ozone, and equations for determination of quantum yield of dichlorine heptoxide formation and ozone decomposition.

EVALUATION OF THE MECHANISM

The proposed mechanism consists of a primary process where chlorine absorbs a quantum of energy to produce two chlorine atoms, six thermal secondary reactions, four which lead to production of dichlorine heptoxide, and six which lead to ozone decomposition, and 22 side reactions. This section will evaluate the mechanism. It will first establish which side reactions are significant. Then it will present an acceptable mechanism and the resultant equations for the rate of formation of dichlorine heptoxide and decomposition of ozone and the quantum yield of dichlorine heptoxide formation and ozone decomposition. Using certain known and estimated rate constants, the mechanism will be shown to follow the data obtained in the experimental study. Estimates of the rate

of decomposition of ozone in the present system will be used to obtain quantum yields of ozone decomposition and these values will be discussed in light of the proposed mechanism, experimental evidence, and results of previous workers.

Elimination of Side Reactions

The side reactions, presented in Table XVII, were considered on the basis that they were discussed or suggested by previous authors and were acceptable in light of current understanding. Most of these reactions can be eliminated as major contributing steps by consideration of the reacting conditions, concentrations, and rates of the reactions in question. Equations (77) through (84) definitely occur in the system and represent the recombination of chlorine atoms due to oxygen. In order to simplify the treatment of the reaction mechanism which would allow determination of rate and quantum yield expressions, these equations have been replaced with Equation (102),

$$2\ Cl + O_2 \longrightarrow Cl_2 + O_2. \qquad (102)$$

Therefore, Equation (102) represents the recombination of chlorine atoms due to oxygen.

Equations (79), (80), and (81) are included in the mechanism to account for the decomposition of ClO formed in Equation (39) and not used by Equation (40). These equations lead to the 0.5 power relationship with respect to light intensity absorbed when Equations (39) and (40) predominate over Equation (97).

Equation (37) has been eliminated on the basis of the low concentration of atomic chlorine since it competes with Equation (10) for chlorine dioxide. Both reactions have been shown to be fast. The rate constant for Equation (37) is greater than or equal to 5.01×10^8 liters/mole sec. at 294°K as reported by

TABLE XVII

SIDE REACTIONS CONSIDERED IN THE MECHANISM

Equation Number	Equation	Accepted for Mechanism
77	$Cl + O_2 + M \longrightarrow ClOO + M$	No
78	$ClOO + M \longrightarrow Cl + O_2 + M$	No
79	$Cl + ClOO \longrightarrow ClO + ClO$	Yes
80	$ClO + ClO \longrightarrow Cl + ClOO$	Yes
81	$Cl + ClOO \longrightarrow Cl_2 + O_2$	Yes
82	$ClO + ClO + M \longrightarrow Cl_2O_2 + M$	No
83	$Cl_2O_2 + M \longrightarrow ClO + ClO + M$	No
84	$Cl_2O_2 + M \longrightarrow Cl_2 + O_2 + M$	No
37	$ClO_2 + Cl \longrightarrow 2\ ClO$	No
59	$ClO_2 + h\nu \longrightarrow ClO + O$	No
75	$ClO_2 + O \longrightarrow ClO + O_2$	No
60	$ClO_2 + O + M \longrightarrow ClO_3 + M$	No
33	$2\ ClO_3 \longrightarrow 2\ ClO_2 + O_2$	No
38	$ClO_3 + Cl \longrightarrow ClO_2 + ClO$	No
11	$ClO_3 + O_3 \longrightarrow ClO_2 + 2\ O_2$	No
76	$ClO_3 + h\nu \longrightarrow ClO_2 + O$	No
13	$2\ ClO_3 \longrightarrow Cl_2O_6$	No
99	$ClO + O \longrightarrow Cl + O_2$	No
56	$Cl_2 + O \longrightarrow ClO + Cl$	No
100	$2\ Cl + Cl_2 \longrightarrow 2\ Cl_2$	Yes
101	$2\ Cl + He \longrightarrow Cl_2 + He$	Yes
74	$Cl \xrightarrow{\text{wall}} 1/2\ Cl_2$	Yes

Coxon (48). Since the concentration of ozone in the system is 8.82×10^{-3} moles/liter, and that of the chlorine atom, as later calculations based on the reaction zone will show, is of the order of $3.0\text{-}9.0 \times 10^{-9}$ moles/liter, Equation (10) will take precedence over Equation (37) even if the rate constant of Equation (10) is of the order of 10^3 liters/mole sec. It seems highly unlikely that the rate constant of Equation (10) would be less than 10^3 liters/mole sec. since it is considered a very fast reaction with little temperature dependence.

Equation (59) has also been eliminated based primarily on the fact that the chlorine dioxide concentration is much less than the chlorine concentration. The chlorine concentration is 8.82×10^{-3} moles/liter. The chlorine dioxide concentration is estimated as less than 9.0×10^{-9} moles/liter. The chlorine dioxide concentration is based on the chlorine atom concentration since it is directly related through Equations (97) and (98). The extinction coefficient of chlorine dioxide in carbon tetrachloride at 365 nm. has been shown to be at least ten times greater than chlorine by Spurry (80). The combination of the difference in concentration and difference in extinction coefficient means that chlorine absorbs approximately 1.0×10^5 more quanta of light than chlorine dioxide. Since the intensity of the light entering the reactor is 3.05×10^{15} quanta/sec., this means only 3.0×10^{10} quanta/sec. is expected to be absorbed by the chlorine dioxide with resultant decomposition, or 5.0×10^{-14} moles of chlorine dioxide destroyed per second. As Table XVI indicates the total moles of dichlorine heptoxide formed is 6.5×10^{-5} or a formation rate of 1.81×10^{-9} moles/sec. From Equations (10) and (51) it can be seen that on a mole basis the rate of destruction of chlorine dioxide is at least twice as great as the rate of formation of dichlorine heptoxide. Therefore, the rate of destruction of chlorine dioxide by Equation (10) is at least

3.62×10^{-9} moles/sec. and the rate of destruction of chlorine dioxide, 5.0×10^{-14} moles/sec., by Equation (59) is therefore negligible. Equation (76) is thrown out through the use of the same reasoning since the extinction coefficient of chlorine trioxide is less than that for chlorine and its concentration is not more than 2.0×10^{-6} moles/liter.

Equation (59) has been eliminated because of its minute overall rate. Therefore, the rate of production of oxygen atom is very small and subsequent reactions of this species with chlorine, ClO, and chlorine dioxide will also be very small. Therefore, Equations (75), (60), (99), and (56) are considered negligible.

Equation (33) has been eliminated because it is essentially a thermal degradation reaction. Since the temperature of the study was selected to minimize this problem and because the system showed no temperature dependence, this reaction was eliminated from the mechanism.

Equation (38) has been eliminated basically because of the low concentration of reactants. Also in Byrns' work (41) this particular reaction appeared slow, since it was carried out in the presence of dichlorine hexoxide insuring a maximum concentration of chlorine trioxide in the vapor and the rate was easily determinable at 0°C.

Equation (11) was eliminated from the mechanism because the step of ozone colliding with chlorine trioxide is essential in product forming Equation (51). This step has been suggested as producing a long-lived complex between ozone and chlorine trioxide. Though the breakdown of the complex to chlorine dioxide and oxygen may occur, it appears that this may require excessive atomic rearrangement so that the pathway to dichlorine heptoxide formation would be several orders of magnitude greater.

Equation (13), which is the condensation of chlorine trioxide gas to its liquid dimer, has been eliminated because of the observation that no dichlorine hexoxide was found and because the concentration level of chlorine trioxide in the system has been shown to be undetectable.

Therefore, all suggested side reactions have been eliminated except for Equations (100), (101), and (74), which account for the recombination of chlorine atoms due to chlorine, He, and the wall of the vessel.

Equation (102) which accounts for the recombination of chlorine atoms due to oxygen has been used to replace Equations (77) through (84) which are assumed to be in steady state. Equations (79), (80), and (81) have been retained even though in steady state to account for the decomposition of ClO formed by Equation (39) and not used by Equation (40).

Final Mechanism

After elimination of side reactions the proposed mechanism becomes:

$$Cl_2(^1\Sigma_g^+) + h\nu \longrightarrow Cl_2(^3\pi_{o+u}) \longrightarrow Cl(^2P_{3/2}) + Cl(^2P_{1/2}) \quad (17)$$

$$Cl + O_3 + M \longrightarrow ClOOO + M \quad (97)$$

$$ClOOO + O_3 \longrightarrow ClO_2 + 2\,O_2 \quad (98)$$

$$ClO_2 + O_3 \longrightarrow ClO_3 + O_2 \quad (10)$$

$$2\,ClO_3 + O_3 \longrightarrow Cl_2O_7 + O_2 \quad (51)$$

$$Cl + O_3 \longrightarrow ClO + O_2 \quad (39)$$

$$ClO + O_3 \longrightarrow Cl + 2\,O_2 \quad (40)$$

$$ClO + ClO \longrightarrow Cl + ClOO \quad (80)$$

$$Cl + ClOO \longrightarrow ClO + ClO \quad (79)$$

$$Cl + ClOO \longrightarrow Cl_2 + O_2 \quad (81)$$

$$2\,Cl + Cl_2 \longrightarrow 2\,Cl_2 \quad (100)$$

$$2\,Cl + O_2 \longrightarrow Cl_2 + O_2 \quad (102)$$

$$2\,Cl + He \longrightarrow Cl_2 + He \quad (101)$$

$$Cl \xrightarrow{\text{wall}} 1/2\,Cl_2. \quad (74)$$

Using the steady-state assumption for Cl, ClO, ClOO, ClO_2, ClOOO, and ClO_3, the following equations were developed:

$$\frac{d[Cl]}{dt} = 2I_{abs} + k_{40}[ClO][O_3] + k_{80}[ClO]^2 - k_{97}[Cl][O_3][M] - k_{39}[Cl][O_3] - k_{79}[Cl][ClOO] - k_{81}[Cl][ClOO] - 2k_{100}[Cl]^2[Cl_2] - 2k_{102}[Cl]^2[O_2] - 2k_{101}[Cl]^2[He] - k_{74}[Cl] = 0 \quad (103)$$

$$\frac{d[ClO]}{dt} = k_{39}[Cl][O_3] + 2k_{79}[Cl][ClOO] - k_{40}[ClO][O_3] - 2k_{80}[ClO]^2 = 0 \quad (104)$$

$$\frac{d[ClOO]}{dt} = k_{80}[ClO]^2 - k_{79}[Cl][ClOO] - k_{81}[Cl][ClOO] = 0 \quad (105)$$

$$\frac{d[ClO_2]}{dt} = k_{98}[ClOOO][O_3] - k_{10}[ClO_2][O_3] = 0 \quad (106)$$

$$\frac{d[ClOOO]}{dt} = k_{97}[Cl][O_3][M] - k_{98}[ClOOO][O_3] = 0 \quad (107)$$

$$\frac{d[ClO_3]}{dt} = k_{10}[ClO_2][O_3] - 2k_{51}[ClO_3]^2[O_3] = 0. \quad (108)$$

Since the basic equation for the rate of formation of dichlorine heptoxide is

$$\frac{d[Cl_2O_7]}{dt} = k_{51}[ClO_3]^2[O_3], \quad (109)$$

the substitution of Equations (106), (107), and (108) give Equation (110),

$$\frac{d[Cl_2O_7]}{dt} = 1/2\ k_{97}[Cl][O_3][M]. \qquad (110)$$

Equation (111) is the basic equation for decomposition of ozone,

$$\frac{-d[O_3]}{dt} = k_{97}[Cl][O_3][M] + k_{98}[ClOOO][O_3] + k_{10}[ClO_2][O_3] + k_{51}[ClO_3]^2[O_3] + k_{39}[Cl][O_3] + k_{40}[ClO][O_3]. \qquad (111)$$

Equation (111) can be simplified to Equation (112),

$$\frac{-d[O_3]}{dt} = (7/2)k_{97}[Cl][O_3][M] + k_{39}[Cl][O_3] + k_{40}[ClO][O_3]. \qquad (112)$$

From Equations (103) and (105) Equation (113) can be developed,

$$2I_{abs} + k_{40}[ClO][O_3] = k_{97}[Cl][O_3][M] + k_{39}[Cl][O_3] + 2k_{100}[Cl]^2[Cl_2] + 2k_{102}[Cl]^2[O_2] + 2k_{101}[Cl]^2[He] + k_{74}[Cl]. \qquad (113)$$

Equation (113) is then used to develop Equation (114) which expresses the concentration of chlorine atoms,

$$[Cl] = \frac{2I_{abs} + k_{40}[ClO][O_3]}{k_{97}[O_3][M] + k_{39}[O_3] + 2k_{100}[Cl][Cl_2] + 2k_{102}[Cl][O_2] + 2k_{101}[Cl][He] + k_{74}}. \qquad (114)$$

The only chlorine oxide present in Equations (112) and (114) is ClO. Since from Equation (105) the following can be written,

$$[ClOO] = \frac{k_{80}[ClO]^2}{(k_{79} + k_{81})[Cl]}, \qquad (115)$$

this can be substituted into Equation (104) and rearrangement gives Equation (116),

$$2k_{80}[ClO]^2 = \frac{2k_{79}k_{80}}{k_{79} + k_{81}}[ClO]^2 = k_{39}[Cl][O_3] - k_{40}[ClO][O_3]. \qquad (116)$$

However, rate constants of $\underline{k}_{79} = 1.44 \times 10^{-12}$ cc./molecule sec., $\underline{k}_{80} = 6.3 \times 10^{-15}$ cc./molecule sec., and $\underline{k}_{81} = 1.56 \times 10^{-10}$ cc./molecule sec., found in Table XI, page 7725 of Johnston, et al. (35), show that the term $\underline{k}_{79}\underline{k}_{80}/(\underline{k}_{79} + \underline{k}_{81})$ is negligible compared to $2\underline{k}_{80}$. Therefore, Equation (116) can be changed to give the following expression for the concentration of ClO,

$$[ClO] = \sqrt{\frac{k_{39}[Cl][O_3] - k_{40}[ClO][O_3]}{2k_{80}}}. \qquad (117)$$

Using Equations (110) and (114) a general form of the rate equation of formation of dichlorine heptoxide can be obtained,

$$\frac{d[Cl_2O_7]}{dt} = \left[k_{97}[O_3][M](2I_{abs} + k_{40}[ClO][O_3])\right] \div \left[2(k_{97}[O_3][M] + k_{39}[O_3] + 2k_{100}[Cl][Cl_2] + 2k_{102}[Cl][O_2] + 2k_{101}[Cl][He] + k_{74})\right]. \qquad (118)$$

The quantum yield of dichlorine heptoxide formation becomes

$$\phi_{Cl_2O_7} = \left[k_{97}[O_3][M](2I_{abs} + k_{40}[ClO][O_3])\right] \div \left[2I_{abs}(k_{97}[O_3][M] + k_{39}[O_3] + 2k_{100}[Cl][Cl_2] + 2k_{102}[Cl][O_2] + 2k_{101}[Cl][He] + k_{74})\right]. \qquad (119)$$

The equation for the rate of decomposition of O_3 becomes

$$\frac{-d[O_3]}{dt} = \left[(7/2\ k_{97}[O_3][M] + k_{39}[O_3])(2I_{abs} + k_{40}[ClO][O_3])\right]$$

$$\div \left[(k_{97}[O_3][M] + k_{39}[O_3] + 2k_{100}[Cl][Cl_2] + 2k_{102}[Cl][O_2] + 2k_{101}[Cl][He] + k_{74})\right]$$

$$+ k_{40}[O_3] \sqrt{\frac{k_{39}[Cl][O_3] - k_{40}[ClO][O_3]}{2k_{80}}}, \qquad (120)$$

and the equation for the quantum yield of decomposition of O_3 becomes

$$\phi_{O_3} = \left(\frac{-d[O_3]}{dt}\right)/I_{abs}. \qquad (121)$$

Although quite complex these rate and quantum yield equations account for all the evidence determined about the system in the present study and by past workers. By simplifying these equations to account for the extreme cases this can be shown more readily.

First consider the case where the ozone concentration is high but the chlorine and oxygen concentrations are low. Under these conditions as has been previously noted the rate of decomposition of ozone becomes a chain mechanism which has some dependence on ozone, and has a $\underline{I}^{0.5}$ relationship. The quantum yield approaches a $\underline{I}^{-0.5}$ relationship. Under these conditions, Equation (114) can be simplified to,

$$[Cl] = \frac{2I_{abs} + k_{40}[ClO][O_3]}{k_{39}[O_3] + k_{74}}, \qquad (122)$$

because recombination of chlorine atoms due to chlorine, oxygen, and He is negligible and Equation (97) is negligible compared to Equation (39). Equation (112) can be simplified to,

$$\frac{-d[O_3]}{dt} = k_{39}[Cl][O_3] + k_{40}[ClO][O_3], \tag{123}$$

since the rate of decomposition of ozone is now influenced by the chain mechanism set up by Equations (39) and (40) and because Equation (97) is now negligible compared to Equations (39) and (40). The rate of decomposition of ozone can then be expressed in the following form:

$$\frac{-d[O_3]}{dt} = \frac{k_{39}[O_3](2I_{abs} + k_{40}[ClO][O_3])}{k_{39}[O_3] + k_{74}} + k_{40}[O_3][ClO]. \tag{124}$$

The quantum yield of ozone decomposition under these conditions becomes,

$$\phi_{O_3} = \frac{2k_{39}[O_3]}{k_{39}[O_3] + k_{74}} + \frac{k_{39}k_{40}[ClO][O_3]^2}{I_{abs}(k_{39}[O_3] + k_{74})} + \frac{k_{40}[ClO][O_3]}{I_{abs}}. \tag{125}$$

Because of the presence of chlorine atom in Equation (117) it is possible that an $\underline{I}^{-0.5}$ relationship is approached due to the ClO concentration terms.

When the ozone concentration is high along with high chlorine and oxygen concentrations, the rate of ozone decomposition becomes zero order with respect to ozone and proportional to light intensity. The quantum yield expression is independent of light intensity and zero order with respect to ozone. Under these conditions the equation for rate of decomposition of ozone simplifies to

$$\frac{-d[O_3]}{dt} = (7/2)k_{97}[Cl][O_3][M], \tag{126}$$

since Equations (39) and (40) are retarded. It is expected though that they still occur to account for slight increases in pressure. The chlorine atom concentration expression is also changed,

$$[Cl] = \frac{2I_{abs}}{k_{97}[O_3][M] + 2k_{100}[Cl][Cl_2] + 2k_{102}[Cl][O_2] + k_{74}}. \tag{127}$$

Equation (127) substituted into Equation (126) gives an expression of rate of decomposition of ozone proportional to light intensity and approaching zero order with respect to ozone.

$$\frac{-d[O_3]}{dt} = \frac{7\ k_{97}[O_3][M]\ I_{abs}}{k_{97}[O_3][M] + 2k_{100}[Cl][Cl_2] + 2k_{102}[Cl][O_2] + k_{74}}. \qquad (128)$$

The quantum yield for decomposition of ozone then becomes,

$$\phi_{O_3} = \frac{7\ k_{97}[O_3][M]}{k_{97}[O_3][M] + 2k_{100}[Cl][Cl_2] + 2k_{102}[Cl][O_2] + k_{74}}, \qquad (129)$$

which as specified is independent of light intensity and approaches zero order with respect to ozone.

Fitting the Mechanism to Actual Data

As studied in the present investigation, the system had high ozone, and high chlorine concentrations. Diluents, oxygen, and helium, were introduced and their effect on the dichlorine heptoxide formed compared with conditions when no diluent was used. Under these experimental conditions the rate of formation of dichlorine heptoxide can be expressed as

$$\frac{d[Cl_2O_7]}{dt} = \left[k_{97}[O_3][M]\ I_{abs}\right] \div \left[k_{97}[O_3][M] + 2k_{100}[Cl][Cl_2] + 2k_{102}[Cl][O_2] + 2k_{101}[Cl][He] + k_{74}\right] \qquad (130)$$

based on Equation (118) where Equations (39) and (40) are considered negligible, although they are occurring as indicated by slight pressure increases. A later section will discuss Equations (39) and (40) in relationship to ozone decomposition. The rate constants for Equations (100), (101), (102), and (74) can be

found directly from the literature or estimated from literature values while the rate constant for Equation (97) is unknown. The concentrations of chlorine, ozone, and oxygen are known at the beginning of a reaction. The concentrations of ozone, oxygen, and chlorine during and at the end of a reaction can be estimated based on the amount of dichlorine heptoxide formed. The concentration of He is constant throughout the reaction. The only other unknown is the chlorine atom concentration. A trial and error procedure was then followed to obtain estimates of k_{97} and chlorine atom concentrations which lead to a plot of perchlorate formed versus time which was similar to that obtained by actual experiment. The concentrations were based on the volume (0.6116 liter) of the whole reactor for chlorine, ozone, helium, and oxygen, and on the estimated volume of the reaction zone (0.155 liter) for chlorine atom. The smaller volume was used for chlorine atoms since this is the portion of the reactor where the chlorine atoms are actually being produced by the light beam. In other parts of the reactor, chlorine atoms will undergo fairly rapid recombination and thus will have a negligible concentration. The concentration found for chlorine atoms in this smaller portion of the reactor is an average concentration since it is expected that the concentration of chlorine atoms will be higher within the light beam and lower in areas out of the light beam.

The front portion of the reactor or reaction zone, volume 0.155 liter, is where the bulk of the reaction is assumed to take place. Therefore, the rate constant for recombination of chlorine atoms at the wall, k_{74}, is based on the surface area available in the reaction zone and not the surface area of the whole reactor. The rate constant expressed for Equation (97) is thus dependent on the volume chosen for the reaction zone. It will be shown that if the entire volume of the reactor is considered the rate constant for Equation (97) is lowered.

Further consideration of Equation (97) shows that it actually represents four individual reactions.

$$Cl + 2\ O_3 \longrightarrow ClOOO + O_3 \qquad (131)$$

$$Cl + O_3 + Cl_2 \longrightarrow ClOOO + Cl_2 \qquad (132)$$

$$Cl + O_3 + O_2 \longrightarrow ClOOO + O_2 \qquad (133)$$

$$Cl + O_3 + He \longrightarrow ClOOO + He \qquad (134)$$

In Equations (131), (132), (133), and (134) the M of Equation (97) is replaced by O_3, Cl_2, O_2, and He, respectively. Therefore, anywhere that Equation (97) appears any of the above reactions can be substituted if the particular third body is present. It is also expected that ozone, chlorine, oxygen, and He will have different efficiencies as far as fulfilling the task of carrying off energy. In the three systems studied, ozone and chlorine are common and have the same ratio. Therefore, Equation (135) has been proposed,

$$Cl + O_3 + M' \longrightarrow ClOOO + M', \qquad (135)$$

where M' is the sum of the ozone and chlorine concentrations. Under the conditions studied, estimates of k_{133}, k_{134}, and k_{135} have been made. Table XVIII presents these rate constants. Appendix XII presents the method of calculation and sample calculations. Table XIX presents the results of a series of calculations based on the above rate constants, when He is used as the diluent at 0°C. Figure 15 presents the total moles of perchlorate formed according to the calculations versus time of reaction on the same axes as the actual data, along with the regression line of the actual data. It can be seen that the calculated points fit well and are within the experimental error experienced for actual data through at least 15 hours. These points could be made to fit the data even better if the values for k_{133} and k_{135} were increased. Also found in

Appendix XII are the rate constants and subsequent results of calculations obtained when the entire reactor volume is considered the reaction zone.

TABLE XVIII

RATE CONSTANTS USED IN CALCULATIONS AT 0°C.

Equation Number	Equation	Rate Constant	Reference[a]
100	$2\ Cl + Cl_2 \longrightarrow 2\ Cl_2$	2.0×10^{10} liter^2/mole^{2}sec.	(25)
101	$2\ Cl + He \longrightarrow Cl_2 + He$	4.25×10^{9} liter^2/mole^{2}sec.	(25)
74	$Cl \xrightarrow{wall} 1/2\ Cl_2$	0.93 sec.$^{-1}$[b]	(81)
102	$2\ Cl + O_2 \longrightarrow Cl_2 + O_2$	2.05×10^{11} liter^2/mole^{2}sec.	(35)
133	$Cl + O_3 + O_2 \longrightarrow ClOOO + O_2$	5.0×10^{4} liter^2/mole^{2}sec.[b]	
134	$Cl + O_3 + He \longrightarrow ClOOO + He$	$<1.0 \times 10^{2}$ liter^2/mole^{2}sec.[b]	
135	$Cl + O_3 + M' \longrightarrow ClOOO + M'$	2.2×10^{4} liter^2/mole^{2}sec.[b]	

[a]The reference given is that from which the basic data were obtained. Appendix XII will further explain any necessary calculations and the temperature at which the rate constants were measured.

[b]Based on reaction zone of 0.155 liter.

Although the proposed mechanism appears to explain the data, it is not necessarily the true mechanism. If it is accepted along with the resultant calculations then it points out some interesting aspects of the system which were not evident from the data obtained. First, there is the complex manner in which third bodies affect the system by causing the recombination of chlorine atoms and stabilization of the chlorine atom-ozone complex (ClOOO); therefore, they act to decrease the rate of formation of dichlorine heptoxide in one manner and increase it in another. The calculations also indicate a product versus time curve that is not linear but is slightly curved. However, the curvature

TABLE XIX

INSTANTANEOUS REACTION RATES AND QUANTUM YIELDS AT 0°C.

Time, hr.	Species Concentration,[a] moles/liter $O_3 \times 10^3$	$Cl_2 \times 10^3$	$He \times 10^3$	$O_2 \times 10^4$	$Cl \times 10^9$	$Cl_2O_7 \times 10^4$	ClO_4^- Formed, moles $\times 10^4$	Reaction Rate,[b] mole/liter sec. $\times 10^8$	Quantum Yield of Cl_2O_7 Formation
				Helium as Diluent					
0	8.82	8.82	8.82	0	8.28	0	0	1.42	0.433
$\frac{1}{2}$	8.77	8.81	8.82	0.45	8.19	0.06	0.08	1.40	0.428
1	8.73	8.81	8.82	0.90	8.10	0.13	0.16	1.38	0.421
2	8.64	8.79	8.82	1.78	7.90	0.25	0.31	1.34	0.410
4	8.47	8.77	8.82	3.50	7.58	0.50	0.61	1.28	0.391
7	8.23	8.74	8.82	5.95	7.22	0.85	1.04	1.20	0.366
10	8.00	8.70	8.82	8.25	6.91	1.18	1.44	1.13	0.346
15	7.63	8.65	8.82	11.9	6.52	1.69	2.08	1.04	0.317
20	7.30	8.60	8.82	15.2	6.22	2.17	2.66	0.97	0.295
26	6.93	8.55	8.82	18.9	5.94	2.70	3.30	0.89	0.273
				No Diluent					
0	8.82	8.82	0	0	8.78	0	0	1.50	0.459
10	7.71	8.73	0	12.9	6.55	1.19[c]	1.46±0.14[c]	1.08	0.330
				O_2 as Diluent					
0	8.82	8.82	0	88.2	3.16	0	0	1.15	0.352
10	7.94	8.76	0	98.8	3.07	0.99[c]	1.21±0.14[c]	1.05	0.322

[a] Concentration of O_3, Cl_2, He, O_2, and Cl_2O_7 based on 0.6116 liter, concentration of Cl based on 0.155 liter reaction zone.

[b] Reaction rate based on reaction zone of 0.155 liter.

[c] These are actual experimental values, not from calculations.

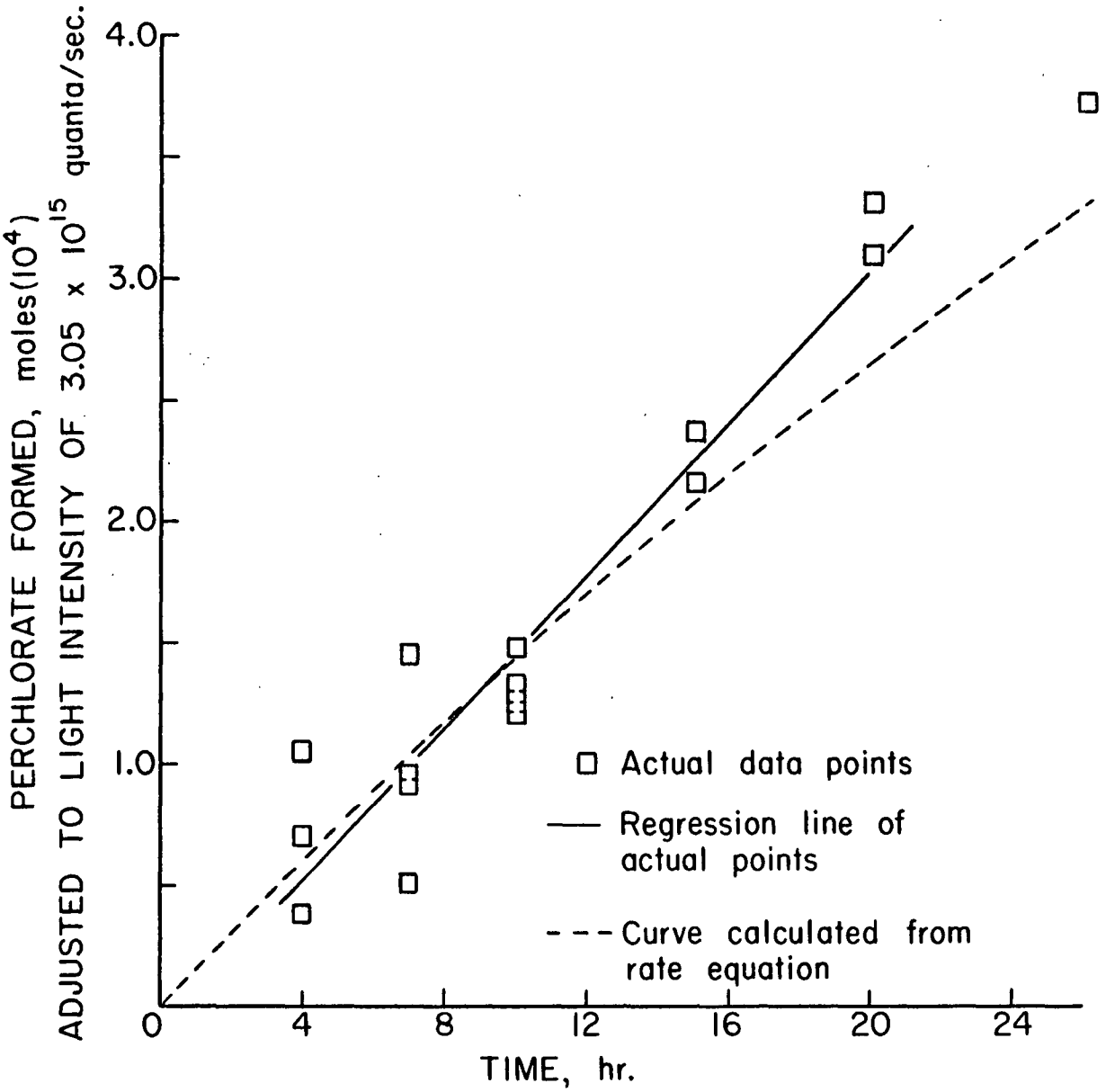


Figure 15. Moles of Perchlorate Formed vs. Time at 0°C.: Actual Data and Calculated Curve.

is so slight that it cannot be detected with the present system. Therefore, the rates obtained from the experiments are average rates over the period of time studied while the calculations give an instantaneous rate. For example, the average rate of formation of dichlorine heptoxide with He as diluent from the calculations for the first 10 hours is 1.28×10^{-8} moles/liter sec., Table XIX, which is comparable to the $1.16 \pm 0.13 \times 10^{-8}$ moles/liter sec. found in Table XVI. The rate constants obtained for Equations (133), (134), and (135) indicate that oxygen is much more efficient in carrying away energy than ozone, chlorine, and He as is the case when oxygen, chlorine, and He are used to recombine chlorine atoms. In fact the rate constant given for Equation (134) is negligible in the calculations.

Effect of Involved Reactions on Quantum Yield of Cl_2O_7 Formation

The calculations also show the effect of the various reactions on the quantum yield for the formation of dichlorine heptoxide. Equation (136) is based on Equation (119) simplified for the conditions of the experiment,

$$\phi_{Cl_2O_7} = \frac{ABC}{ABC + 2k_{100}[Cl][Cl_2] + 2k_{102}[Cl][O_2] + 2k_{101}[Cl][He] + k_{74}}, \qquad (136)$$

where $\underline{ABC} = \underline{k}_{135}[O_3][\underline{M}'] + \underline{k}_{133}[O_3][O_2] + \underline{k}_{134}[O_3][He]$. Obviously, Equations (135), (133), and (134) are directly involved with formation of dichlorine heptoxide while Equations (100), (101), (102), and (74) act to recombine chlorine atoms and decrease the efficiency of the reaction. Table XIX shows that the quantum yield of dichlorine heptoxide formation decreases throughout the reaction from 0.433 at 0 time to 0.273 after 26 hours. Table XX shows the effect of each of these reactions in using the energy supplied by the light source. The first part of the table shows the data of the O_3, Cl_2, He system, the second

part the O_3, Cl_2 system, and the last part the O_3, Cl_2, O_2 system. Equation (134) does not appear because its effect has been shown to be negligible.

TABLE XX

PERCENTAGE OF LIGHT ENERGY ABSORBED USED BY DIFFERENT EQUATIONS

Time, hr.	Percent Effect of Indicated Equation					
	(135)	(133)	(100)	(102)	(101)	(74)
			O_3, Cl_2, He System			
0	43.3	0	37.0	0	7.9	11.8
1	41.6	0.5	35.2	3.7	7.5	11.5
2	40.1	0.9	33.6	7.0	7.1	11.3
4	37.4	1.7	30.9	12.6	6.6	10.8
7	34.0	2.6	27.8	19.4	6.0	10.2
10	31.1	3.5	25.4	24.7	5.5	9.8
15	27.2	4.5	22.5	31.6	4.9	9.3
20	24.3	5.2	20.4	36.8	4.5	8.8
26	21.4	5.9	18.5	41.8	4.0	8.4
			O_3, Cl_2 System			
0	45.9	0	41.6	0	--	12.5
10	28.0	5.0	23.0	34.7	--	9.3
			O_3, Cl_2, O_2 System			
0	16.5	18.7	5.4	54.9	--	4.5
10	13.7	18.5	5.0	58.4	--	4.4

Table XX established some very interesting points about the system. The most important is the effect of oxygen in the system. Even in those systems where oxygen is not present originally its effect becomes substantial after a period of 10 hours. In the systems where oxygen is the diluent, Equation (133) predominates over (135) for eventual formation of dichlorine heptoxide and Equation (102) is the major source of chlorine atom recombination. The chlorine atom recombination at the wall is fairly stable in each system. The major fluctuations are due to Equation (135) because of decrease in the concentration of ozone and chlorine and Equation (100) whose effect on chlorine atom recombination is decreased markedly as Equation (102) becomes predominant. The effect of He is very small even in chlorine atom recombination.

Rate of Decomposition of O_3 and its Quantum Yield

As stated earlier, the final concentration of ozone in the experimental system could not be determined with the chemical methods tried. The conditions used in the experiments were such that Equations (39) and (40) were decreased to a minimum. Film formation on the walls of the reactor left pressure measurements as a means of indicating ozone decomposition somewhat in doubt. Therefore, an evaluation of the rate constants for Equations (39) and (40) will not be attempted. However, from Equation (126) it is seen that the rate of ozone decomposition is at least seven times the rate of dichlorine heptoxide formation. Therefore, knowing the rate of dichlorine heptoxide formation and using the slight pressure increase in the system, one can estimate the ozone decomposed and obtain quantum yields of ozone decomposition. These quantum yields can then be compared with those in the literature. Table XXI presents these data for the three systems studied: Cl_2, O_3; Cl_2, O_3, He; and Cl_2, O_3, O_2.

These quantum yields of ozone decomposition compare well with those found in the literature. Allmand and Spinks (37,38) reported 2.6 for decomposition initiated by light of 365 nm. under conditions where chain breakdown of ozone was retarded. Norrish and Neville (49) reported quantum yields of destruction of ozone as reaching a limiting value of 2 as chlorine and oxygen concentrations increased. Norrish and Neville also reported quantum yields as high as 10 according to the conditions of the experiment. It is expected that due to film formation in the reactor during the present study, and because Equation (39) gives no net change in moles, that the actual quantum yield is higher than that given by as much as two times. Even then the quantum yield falls within the expected region.

TABLE XXI

RATE OF OZONE DECOMPOSITION AND QUANTUM YIELD, AT 0°C.
AVERAGE DATA OVER 10-HOUR RUN

System	Ozone Decomposition, moles/liter sec. (10^8) From Cl_2O_7 Formation Data	From Pressure Rise Data	Total	Quantum Yield of O_3 Decomposition
O_3, Cl_2	2.32	0.85	3.17	3.82
O_3, Cl_2, He	2.07	0.19	2.26	2.72
O_3, Cl_2, O_2	1.93	0.61	2.54	3.06

Further consideration of the data in Table XXI indicates that the O_3, Cl_2 system gives more decomposition of ozone. This is expected since the total pressure in the system is lower (less third bodies), causing a greater tendency for the ozone to decompose through the chain mechanism. The data also indicate that the O_3, Cl_2, O_2 system gives greater decomposition of ozone than the O_3, Cl_2, He system, despite the fact that the total pressure is the same. This is

believed to be caused by the presence of a higher concentration of ClO in the O_3, Cl_2, O_2 system as shown in Appendix XIII. This higher concentration of ClO causes an increase in the rate of decomposition of ozone through Equation (40).

LITERATURE CONTRADICTIONS

The new experimental evidence about the chlorine-ozone photochemical system, the proposed mechanism, and manipulation of the mechanism through calculations appear to agree almost entirely with evidence obtained by previous investigators with a few exceptions. Norrish and Neville (49) followed the decomposition of ozone through pressure measurements. They reported no effect on the decomposition of ozone due to introduction of nitrogen and carbon dioxide. In the present study the results indicate a slight decrease in the rate of formation of dichlorine heptoxide and thus the decomposition of ozone due to addition of He. It is believed that nitrogen and carbon dioxide also have a slight effect which was undetected by Norrish and Neville. This reasoning is based on the results of Porter and Wright (82) who found that the rate of recombination of chlorine atoms in oxygen is 46 times faster than in nitrogen. Therefore, by referring to Table XVIII, it is seen that nitrogen is about as efficient as He in the recombination of chlorine atoms. Thus, it is expected that nitrogen will act like He and only affect the system in a very small way. It is assumed that carbon dioxide acts in the same manner as nitrogen.

Using pressure measurements to follow the reaction, previous workers reported an induction period. An induction period could not be substantiated in this work because of the accuracy of the data and the possibility that the induction period was short (less than one hour). The mechanism and subsequent calculations indicate no induction period. However, these calculations are based on an already established equilibrium of intermediates. The pressure

measurements did, however, show a slight negative change during the first four hours of the experimental runs. This early decrease in pressure has been attributed to film formation on the walls of the reaction vessel. If previous workers had any film formation or preferential absorption of intermediates and products on the reactor wall, this could account for an apparent induction period as observed from pressure data in contrast to one which requires establishment of equilibrium concentrations of intermediates.

The biggest contradiction between this work and that of the earlier workers is the finding of dichlorine heptoxide as the only product of the reaction. Earlier workers had reported both dichlorine hexoxide and dichlorine heptoxide as forming in measurable quantities. The reason for this discrepancy is based on the concentration of chlorine trioxide, and the subsequent condensation of dichlorine hexoxide. Although the earlier workers reported mixtures of dichlorine hexoxide and dichlorine heptoxide, they gave no quantitative evidence of the amounts formed or their ratio. Therefore, there is the possibility that the color of a small amount of dichlorine hexoxide, an oily red liquid, could make a large amount of dichlorine heptoxide, an oily colorless liquid, appear to them to be a large amount of dichlorine hexoxide. It is possible that in the present study certain characteristics of the experimental system lowered the overall concentration of chlorine trioxide, resulting in no appearance of an oily red liquid and in no detection of chlorine trioxide through formation of the chlorate ion in water.

The possible reasons for this lowering of concentration of chlorine trioxide are as follows:

1. The presence of teflon in the system could cause a surface effect which increases the rate of some of the side reactions involving chlorine trioxide.

2. The divergent nature of the light beam could cause decomposition of dichlorine hexoxide on the walls of the reactor.

3. The high light intensity in the reaction zone may act to photochemically destroy chlorine trioxide.

4. The rate of formation of dichlorine heptoxide may be enhanced in some manner so that the concentration of chlorine trioxide is lowered.

Of the possible reasons given, number four seems most appropriate. If the rate of formation of dichlorine heptoxide is enhanced in some manner, then the overall concentration of chlorine trioxide may be lowered to the point where it is not detected. Equation (51),

$$2\ ClO_3 + O_3 \longrightarrow Cl_2O_7 + O_2, \qquad (51)$$

shows the formation of dichlorine heptoxide with the removal of two molecules of chlorine trioxide. To increase the rate of this reaction, the concentration of chlorine trioxide, ozone, or both would have to be increased. In the system studied the ozone concentration is at least as high as in the earlier work. The light intensity is also at a level as high as in the earlier work. Because of the light intensity being at a high level there is the possibility of having a locally high concentration of chlorine trioxide within the reaction zone. Therefore, Equation (51) would be enhanced due to the concentration of chlorine trioxide and ozone. In this case the overall concentration of chlorine trioxide would not reach a detectable level.

The other possible reasons for the overall lowering of the chlorine trioxide concentration were considered using the following logic: (1) the presence of a surface effect due to teflon was ruled out because of the relatively small

surface area of the teflon and because the teflon is in a part of the reactor considered not to be in the reaction zone; (2) an effect due to the divergent nature of the light beam was ruled out because visual observation of the film formed on the walls of the reactor gave no evidence of a difference in the film where it was struck by light; furthermore most of the light is absorbed before reaching the walls of the reactor; and (3) decomposition of chlorine trioxide by light was ruled out as a major reason because of its low extinction coefficient and concentration in relation to chlorine; however, since reason four has been accepted on the premise that there may be a high local concentration of chlorine trioxide then decomposition of chlorine trioxide may become a contributing factor.

CONCLUSIONS

The major chlorine oxide product of the reaction system was found to be dichlorine heptoxide. This is in contradication to what was expected through study of the literature. The rate of formation of dichlorine heptoxide, under the conditions of the experimental work, was found to be directly proportional to the light intensity absorbed, independent of temperature, slightly reduced by the introduction of third bodies, and approaching a zero-order relationship with respect to ozone.

The above evidence was used along with existing literature to develop a reaction mechanism. In this mechanism dichlorine heptoxide is formed through a stepwise nonchain series of reactions involving ozone and a number of intermediate chlorine oxides, ClOOO, chlorine dioxide, and chlorine trioxide. The decomposition of ozone is shown to be a chain mechanism under some but not all reaction conditions. The chain-carrying species has been rationalized as ClO. The key to the mechanism is the formation of a chlorine atom-ozone complex, ClOOO, which can be stabilized by a third body allowing further stepwise production of dichlorine heptoxide or can immediately decompose to ClO and oxygen. The ClO then reacts with ozone to form a chlorine atom and oxygen starting the chain decomposition of ozone.

The development of rate equations and quantum yield equations from the mechanism shows that the mechanism accounts for essentially all of the experimental evidence that has been established about the system. The results of the present study were then used in conjunction with the mechanism and rate equations to estimate the rate constants of three key reactions.

$$Cl + O_3 + O_2 \longrightarrow ClOOO + O_2 \quad (133)$$

$$Cl + O_3 + He \longrightarrow ClOOO + He \quad (134)$$

$$Cl + O_3 + M' \longrightarrow ClOOO + M' \quad (135)$$

M' is the sum of ozone and chlorine where the ratio of the two species is 1. These rate constants are 5.0×10^4, $<1.0 \times 10^2$, and 2.2×10^4 liter^2/mole^2 sec. for Equations (133), (134), and (135), respectively. The mechanism also indicates that third bodies acting in a complex manner can both speed up and slow down the formation of dichlorine heptoxide. They do this by increasing the rate via the above equations and by decreasing the rate, due to lowering of the chlorine atom concentration, via chlorine atom recombination reactions. In either case, ozone, chlorine, and oxygen were shown to be very efficient third bodies while He was shown to be inefficient.

FUTURE WORK

Using the present experimental apparatus, only a minimum amount of information could be obtained about the system. Further study of this system could take two pathways. First, the entire system could be studied using sophisticated analytical techniques such as ultraviolet and infrared spectroscopy which would allow attainment of reactant, product, and intermediate concentrations at any instant in time. Second, individual reactions of the proposed mechanism could be studied. These studies would also require modern analytical techniques. The combination of the two types of study would then give a much broader understanding of the system and allow further refinement of the proposed mechanism.

LIST OF CHEMICAL SYMBOLS AND NAMES

As_2O_3 = Arsenious oxide

$CaCl_2$ = Calcium chloride

CCl_4 = Carbon tetrachloride

Cl = Chlorine atom

Cl^- = Chloride ion

ClO = Chlorine monoxide

ClO^- = Hypochlorite ion

ClOO = Chlorine peroxide

ClO_2 = Chlorine dioxide

ClO_2^- = Chlorite ion

ClOOO = Chlorine atom-ozone complex

ClOOO* = Activated chlorine atom-ozone complex

ClO_3 = Chlorine trioxide

ClO_3* = Activated chlorine trioxide

$\underline{ClO_3}$ = Liquid chlorine trioxide

ClO_3^- = Chlorate ion

ClO_4 = Chlorine tetroxide

ClO_4^- = Perchlorate ion

Cl_2 = Chlorine or chlorine molecule

Cl_2* = Activated chlorine

Cl_2O = Dichlorine monoxide

Cl_2O_2 = Dichlorine dioxide

Cl_2O_3 = Dichlorine trioxide

Cl_2O_6 or $\underline{Cl_2O_6}$ = Dichlorine hexoxide

Cl_2O_7 = Dichlorine heptoxide

Cl_3 = Triatomic chlorine

CO_2 = Carbon dioxide

$CuSO_4$ = Cupric sulfate

$FClO_2$ = Chloryl fluoride

$FClO_4$ = Fluorine perchlorate

Fe^{2+} = Ferrous ion

$FeCl_3$ = Ferric chloride

$Fe(NH_4)_2(SO_4)_2$ = Ferrous ammonium sulfate

$FeSO_4$ = Ferrous sulfate

HCl = Hydrochloric acid

He = Helium

Hg = Mercury

HIO = Hypoiodous acid

H_2O = Water

H_2O_2 = Hydrogen peroxide

H_2SO_4 = Sulfuric acid

H_3PO_4 = Phosphoric acid

I^- = Iodide

I_2 = Iodine

KI = Potassium iodide

$KMnO_4$ = Potassium permanganate

$KReO_4$ = Potassium perrhenate

$K_2C_2O_4$ = Potassium oxalate

$K_3Fe(C_2O_4)_3$ = Potassium ferrioxalate

$NaC_2H_3O_2$ = Sodium acetate

$NaHCO_3$ = Sodium bicarbonate

NaOH = Sodium hydroxide

$Na_2S_2O_3$ = Sodium thiosulfate

N_2 = Nitrogen

O = Oxygen atom

O_2 = Oxygen or oxygen molecule

O_2* = Activated oxygen

O_3 = Ozone

O_3* = Activated ozone

$SnCl_2$ = Stannous chloride

LIST OF CHEMICAL REACTIONS CONSIDERED

$Cl_2 + h\nu \longrightarrow Cl_2^*$ (2)

$Cl_2^* + O_3 \longrightarrow Cl_2 + O_2 + O + \text{energy}$ (3)

$Cl_2^* + O_2 \longrightarrow Cl_2 + O_2^*$ (4)

$O_2^* + O_3 \longrightarrow 2\,O_2 + O + \text{energy}$ (5)

$Cl_2^* \longrightarrow Cl_2 + \text{energy}$ (6)

$O_2^* \longrightarrow O_2 + \text{energy}$ (7)

$O_3 + h\nu \longrightarrow O_3^*$ (8)

$O_3^* + Cl_2 \longrightarrow ClO + ClO_2$ (9)

$ClO_2 + O_3 \longrightarrow ClO_3 + O_2$ (10)

$ClO_3 + O_3 \longrightarrow ClO_2 + 2\,O_2$ (11)

$ClO_3 + ClO_3 \longrightarrow Cl_2 + 3\,O_2$ (12)

$2\,ClO_3 \longrightarrow Cl_2O_6$ (13)

$ClO + ClO \longrightarrow Cl_2 + O_2$ (14)

$Cl_2 + O_3 \longrightarrow ClO + ClO_2$ (15)

$O_3(S_o) + h\nu \longrightarrow O_3(T_1) \longrightarrow O_2(^3\Sigma_g^-) + O(^3P)$ (16)

$Cl_2 + h\nu \longrightarrow 2\,Cl$

$Cl_2 + h\nu \longrightarrow Cl(^2P_{3/2}) + Cl(^2P_{1/2})$ (17)

$Cl_2(^1\Sigma_g^+) + h\nu \longrightarrow Cl_2(^3\pi_{o+u}) \longrightarrow Cl(^2P_{3/2}) + Cl(^2P_{1/2})$

$Cl + O_3 \longrightarrow ClO_3$ (18)

$Cl + O_2 \longrightarrow ClO_2$ (19)

$Cl + O_3 + M \longrightarrow ClO_3^* + M$ (20)

$ClO_3^* \longrightarrow ClO_3$ (21)

$ClO_3 \longrightarrow \underline{ClO_3}$ (22)

$2\,\underline{ClO_3} \longrightarrow Cl_2 + 3\,O_2$ (23)

$2\,\underline{ClO_3} \longrightarrow \underline{Cl_2O_6}$ (24)

$\underline{Cl_2O_6} \longrightarrow Cl_2 + 3\,O_2$ (25)

$ClO_3^* + O_3 \longrightarrow ClO_2 + 2\,O_2$ (26)

$\underline{ClO_3} + O_3 \longrightarrow ClO_2 + 2\,O_2$ (27)

$Cl + O_3 + M \longrightarrow ClO_3 + M$ (28)

$ClO_2 + O_3 \longrightarrow ClO_3^* + O_2$ (29)

$ClO_3^* + M \longrightarrow ClO_3 + M + k.e.$ (30)

$ClO_3^* + O_3 \longrightarrow ClO_4 + O_2$

$ClO_3 + O_3 \longrightarrow ClO_4 + O_2$ (31)

$ClO_3 + ClO_4 \longrightarrow Cl_2O_7$ (32)

$2\,ClO_3 \longrightarrow 2\,ClO_2 + O_2$ (33)

$2\,ClO_3 \longrightarrow ClO_2 + ClO_4$ (34)

$Cl + ClO_3 \longrightarrow Cl_2O_3$ (35)

$Cl + Cl_2O_3 \longrightarrow Cl_2 + Cl + 3/2\,O_2$ (36)

$ClO_2 + Cl \longrightarrow 2\,ClO$ (37)

$ClO_3 + Cl \longrightarrow ClO_2 + ClO$ (38)

$Cl + O_3 \longrightarrow ClO + O_2$ (39)

$ClO + O_3 \longrightarrow Cl + 2\,O_2$ (40)

$Cl + O_3 + Cl_2 \longrightarrow ClO_3 + Cl_2$ (41)

$Cl + O_3 + O_2 \longrightarrow ClO_3 + O_2$ (42)

$Cl + Cl_2 \longrightarrow Cl_3$ (43)

$Cl_3 + O_3 \longrightarrow ClO_3 + Cl_2$ (44)

$ClO + O_3 \longrightarrow ClO_2 + O_2$ (50)

$2\,ClO_3 + O_3 \longrightarrow Cl_2O_7 + O_2$ (51)

$ClO_2 \longrightarrow Cl + O_2$ (52)

$ClO_3 \longrightarrow ClO + O_2$ (53)

$ClO_2 + O_3 \longrightarrow ClO + 2\,O_2$ (54)

$O_3 \longrightarrow O_2 + O$ (55)

$Cl_2 + O \longrightarrow ClO + Cl$ (56)

$O_3 + M \longrightarrow O_2 + O + M$ (57)

$ClO + O_2 \rightleftharpoons ClO_3 \rightleftharpoons 1/2\ Cl_2O_6$ (58)

$ClO_2 + h\nu \longrightarrow ClO + O$ (59)

$ClO_2 + O + M \longrightarrow ClO_3 + M$ (60)

$ClO + ClO_2 \longrightarrow Cl_2O + O_2$ (61)

$O + O + M \longrightarrow O_2 + M$ (62)

$Cl_2O_6 + O \longrightarrow Cl_2O_7$ (63)

$ClO_2 + O \longrightarrow ClO_3$ (64)

$ClO + O_2 \longrightarrow ClO_3$ (65)

$ClO + O_2^* \longrightarrow ClO_3$ (66)

$ClO_3 + h\nu \longrightarrow ClO + O_2^*$ (67)

$2\ ClO_2 \xrightarrow{\text{wall}} ClO + ClO_3$ (68)

$ClO + ClO_2 \longrightarrow Cl_2O_3$ (69)

$ClO + Cl_2O_3 \longrightarrow ClO_2 + ClOOCl$ (70)

$ClOOCl \longrightarrow ClOO + Cl$ (71)

$ClOO \longrightarrow Cl + O_2$ (72)

$ClO_2 + Cl \longrightarrow Cl_2 + O_2$ (73)

$Cl \xrightarrow{\text{wall}} 1/2\ Cl_2$ (74)

$ClO_2 + O \longrightarrow ClO + O_2$ (75)

$ClO_3 + h\nu \longrightarrow ClO_2 + O$ (76)

$Cl + O_2 + M \longrightarrow ClOO + M$ (77)

$ClOO + M \longrightarrow Cl + O_2 + M$ (78)

$Cl + ClOO \longrightarrow ClO + ClO$ (79)

$ClO + ClO \longrightarrow Cl + ClOO$ (80)

$Cl + ClOO \longrightarrow Cl_2 + O_2$ (81)

$ClO + ClO + M \longrightarrow Cl_2O_2 + M$ (82)

$Cl_2O_2 + M \longrightarrow ClO + ClO + M$ (83)

$Cl_2O_2 + M \rightarrow Cl_2 + O_2 + M$ (84)

$2\ Cl + M \rightarrow Cl_2 + M$ (85)

$3\ ClO^- \rightarrow 2\ Cl^- + ClO_3^-$ (86)

$2\ ClO^- \rightarrow 2\ Cl^- + O_2$ (87)

$HClO + ClO^- \rightarrow HClO_2 + Cl^-$ (88)

$ClO^- + HClO_2 \rightarrow HClO_3 + Cl^-$ (89)

$HClO + H^+ + 2I^- \rightarrow Cl^- + H_2O + I_2$ (90)

$I_2 + H_2O \rightarrow H^+ + I^- + HIO$ (91)

$ClO^- + HOI \rightarrow I^- + HClO_2$ (92)

$Cl_2O_7 + H_2O \rightarrow 2\ H^+ + 2\ ClO_4^-$ (93)

$Cl + O_3 \rightarrow ClOOO^*$ (94)

$ClOOO^* \rightarrow ClO + O_2$ (95)

$ClOOO^* + M \rightarrow ClOOO + M$ (96)

$Cl + O_3 + M \rightarrow ClOOO + M$ (97)

$ClOOO + O_3 \rightarrow ClO_2 + 2\ O_2$ (98)

$ClO + O \rightarrow Cl + O_2$ (99)

$2\ Cl + Cl_2 \rightarrow 2\ Cl_2$ (100)

$2\ Cl + He \rightarrow Cl_2 + He$ (101)

$2\ Cl + O_2 \rightarrow Cl_2 + O_2$ (102)

$Cl + 2\ O_3 \rightarrow ClOOO + O_3$ (131)

$Cl + O_3 + Cl_2 \rightarrow ClOOO + Cl_2$ (132)

$Cl + O_3 + O_2 \rightarrow ClOOO + O_2$ (133)

$Cl + O_3 + He \rightarrow ClOOO + He$ (134)

$Cl + O_3 + M' \rightarrow ClOOO + M'$ (135)

where

M' = the sum of the chlorine and ozone concentrations and the ratio of these concentrations must be one.

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LITERATURE CITED

1. Secrist, R. B., and Singh, R. P., Tappi 54, no. 4:581-4(April, 1971).

2. Bolker, H. I., and Liebergott, N., Paper Trade J. 155, no. 50:55(Dec. 13, 1971).

3. Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Supplement II, part I. New York, Longmans, Green and Co., 1956. 1153 p.

4. Farrar, R. L., Jr. Safe handling of chlorine trifluoride and the chemistry of the chlorine oxides and oxyfluorides. AEC Research and Development Report, K-1416, 1960. 33 p.

5. Schmeisser, M., and Brandle, K. Oxides and oxyfluorides of the halogens. In Advances in inorganic chemistry and radiochemistry. Vol. 5. p. 41-89. Emeleus, H. J., and Sharpe, A. G., ed. New York, Academic Press, 1963.

6. Eachus, R. S., Leicester Chemical Review 10:29-39(1969).

7. Pitts, J. N., Wilkinson, F., and Hammond, G. S. The "vocabulary" of photochemistry. In Advances in photochemistry. Vol. 1. p. 1-21. New York, Interscience, 1963.

8. Calvert, J. G., and Pitts, J. N. Photochemistry. New York, John Wiley and Sons, Inc., 1966. 899 p.

9. Farquharson, J., Goodeve, C. F., and Richardson, R. D., Trans. Faraday Soc. 32:790-5(1936).

10. Weigert, F., Ann. Physik. 24:243(1907).

11. Bonhoeffer, K. F., Z. Physik. 13:94-105(1923); C.A. 17:2392.

12. Bodenstein, M., Harteck, P., and Padelt, E., Z. Anorg. u. Allgem. Chem. 147:233-44(1925); C.A. 19:3227.

13. Allmand, A. J., Trans. Faraday Soc. 21:603-6(1926).

14. Durie, R. A., and Ramsey, D. A., Can. J. Phys. 36, no. 1:35-53(Jan., 1958).

15. Walsh, A. D., J. Chem. Soc. 1953:2266-88.

16. Nielsen, A. H., and Woltz, P. J. H., J. Chem. Phys. 20, no. 12:1878-83 (Dec., 1952).

17. Walsh, A. D., J. Chem. Soc. 1953:2301-6.

18. Atkins, P. W., Brivati, J. A., Keen, N., Symons, M. C. R., and Trevalion, P. A., J. Chem. Soc. 1962:4785-93.

19. Venkateswarlu, K., and Rajalakshmi, K. V., Indian J. Pure Appl. Phys. 1, no. 11:380-2(Nov., 1963).

20. Morton, J. R., J. Chem. Phys. 45, no. 5:1800-2(Sept. 1, 1966).

21. Herzberg, G. Molecular spectra and molecular structure. Infrared spectra of diatomic molecules. 2nd ed. New York, Van Nostrand Co., 1950.

22. Dunitz, J. D., and Hedberg, K., J. Am. Chem. Soc. 72, no. 7:3108-12(July, 1950).

23. McHale, E. T., and von Elbe, G., J. Phys. Chem. 72, no. 6:1849-56(June 15, 1968).

24. Akishin, P. A., Vilkov, L. V., and Rosolovsky, B. Ya., Kristallografiya 4:353(1959); Interatomic distances supplement. Special Publication No. 18. London, The Chemical Society, 1965.

25. Hutton, E., and Wright, M., Trans. Faraday Soc. 61:78-89(1965).

26. Tinkham, M., and Strandberg, M. W. P., Phys. Rev. 97, no. 4:951-66(Feb. 15, 1955).

27. Hughes, R. H., J. Chem. Phys. 24, no. 1:131-8(Jan., 1956).

28. Gillespie, R. B., Sparks, R. A., and Trueblood, K. N., Acta Cryst. 12: 867-72(1959).

29. Kartha, G., Acta Cryst. 5:845(1952); Interatomic distances. Special Publication No. 11. London, The Chemical Society, 1958.

30. Lee, F. S., and Carpenter, G. B., J. Phys. Chem. 63, no. 2:279-82(Feb., 1959).

31. Axworthy, A. E., Jr., and Benson, S. W. Mechanism of gas phase decomposition of ozone. Thermal and photochemical reactions. In Ozone chemistry and technology. Advances in Chemistry Series 21, p. 388-97. Washington, American Chemical Society, 1959.

32. Bodenstein, M., and Schumacher, H. J., Z. Physik. Chem. B, 5:233-6(1929).

33. Bodenstein, M., Padelt, E., and Schumacher, H. J., Z. Physik. Chem. 8, no. 5:209-32(1929).

34. Leighton, P. A. Photochemistry of air pollution. p. 47. New York, Academic Press, 1961.

35. Johnston, H. S., Morris, E. D., Jr., and Van den Bogaerde, J., J. Am. Chem. Soc. 91, no. 27:7712-27(Dec. 31, 1969).

36. Allmand, A. J., and Spinks, J. W. T., Nature 124:651(1929).

37. Allmand, A. J., and Spinks, J. W. T., J. Chem. Soc. 1931:1652-66.

38. Allmand, A. J., and Spinks, J. W. T., J. Chem. Soc. 1932:599-612.

39. Heidt, L. J., Kistiakowsky, G. B., and Forbes, G. S., J. Am. Chem. Soc. 55:223-31(1933).

40. Norrish, R. G. W., and Neville, G. H. J., Nature 13:544-5(1933).

41. Byrns, A. C. Some reactions induced by light in mixtures of chlorine and ozone. Doctor's Dissertation. Berkeley, California, University of California, 1934. 56 p.

42. Rollefson, G. K., and Byrns, A. C., J. Am. Chem. Soc. 56:364-7(1934).

43. Byrns, A. C., and Rollefson, G. K., J. Am. Chem. Soc. 56:1250-1(1934).

44. Byrns, A. C., and Rollefson, G. K., J. Am. Chem. Soc. 56:2245-50(1934).

45. Goodeve, C. F., and Powney, J., J. Chem. Soc. 1932:2078-81.

46. Arvia, A. J., Basualdo, W. H., and Schumacher, H. J., Z. Anorg. u. Allgem. Chem. 286:58-80(1956); C.A. 51:2441d.

47. Clyne, M. A. A., and White, I. F., Trans. Faraday Soc. 67, no. 583, Part 7:2068-76(July, 1971).

48. Coxon, J. A., Trans. Faraday Soc. 64, no. 548, Part 8:2118-23(Aug., 1968).

49. Norrish, R. G. W., and Neville, G. H. J., J. Chem. Soc. 1934:1864-72.

50. Goodeve, C. F., and Marsh, A. E. L., J. Chem. Soc. 1939:1332-7.

51. Niki, H., and Weinstock, B., J. Chem. Phys. 47, no. 9:3249-52(Nov. 1, 1967).

52. Szabo, Z. G., J. Chem. Soc. 1950:1356-9.

53. Szabo, Z. G., Acta. Univ. Szegediensis, Acta Chem. et Phys. 3:20-3(1950); C. Z. 45:8386g.

54. Huhn, P., Tudos, F., and Szabo, Z., Magy. Tud. Akad. Kem. Tud. Oszt. Kozlemen. 5:409-18(1954); C.A. 50:41e.

55. JANAF Thermochemical Tables. U.S. National Bureau of Standards, Washington, D.C., U.S. Government Printing Office, 1965.

56. Schumacher, H. J., Z. Phys. Chem. (Frankfurt) 13:353-67(1957).

57. Edgecombe, F. H. C., Norrish, R. G. W., and Thrush, B. A., Chem. Soc. (London), Spec. Publ. No. 9:121-37(1957).

58. McGrath, W. D., and Norrish, R. G. W., Z. Physik. Chem. Neue Folge, 15:245-61(1958).

59. Bowen, E. J., J. Chem. Soc. 123:2328-30(1923).

60. Booth, H., and Bowen, E. J., J. Chem. Soc. 127:510-13(1925).

61. Spinks, J. W. T., J. Am. Chem. Soc. 54:1689-90(1932).

62. Spinks, J. W. T., and Porter, J. M., J. Am. Chem. Soc. 56:264-70(1934).

63. Spinks, J. W. T., and Taube, H., J. Am. Chem. Soc. 59:1155-6(1937).

64. Spinks, J. W. T., and Taube, H., Can. J. Res. 15B, no. 12:499-524(Dec., 1937).

65. Lipscomb, F. J., Norrish, R. G. W., Thrush, F. R. S., and Thrush, B. A., Proc. Roy. Soc. (London) A233, no. 1195:455-64(Jan. 10, 1956).

66. Crawford, R. A., and DeWitt, B. J., Tappi 51, no. 5:226-30(May, 1968).

67. Clyne, M. A. A., and Coxon, J. A., Trans. Faraday Soc. 62, no. 521, Part 5:1175-89(May, 1966).

68. Kalina, M. H., and Spinks, J. W. T., Can. J. Res. 16B, no. 11:381-9 (Nov., 1938).

69. Goodeve, C. F., and Richardson, F. D., Trans. Faraday Soc. 33:453-7(1937).

70. Goodeve, C. F., and Richardson, F. D., J. Chem. Soc. 1937:294-300.

71. Curme, G. O., Jr. Glycols. American Chemical Society Monograph Series No. 114. New York, Reinhold, 1952.

72. Myers, B. F., Bartle, E. R., Erickson, P. R., and Meckstroth, E. A., Anal. Chem. 39, no. 3:415-16(March, 1967).

73. Griggs, M., and Kaye, S., Rev. Sci. Instr. 39, no. 11:1685-6(Nov., 1968).

74. Jenkins, A. C. Laboratory techniques for handling high-concentration liquid ozone. In Ozone chemistry and technology. Advances in Chemistry Series 21. p. 13-21. Washington, American Chemical Society, 1959.

75. Parker, C. A., Proc. Roy. Soc. (London) A220:104-16(1953).

76. Hatchard, C. G., and Parker, C. A., Proc. Roy. Soc. (London) A235:518-36 (1956).

77. Benson, S. W., and Axworthy, A. E., Jr. In Ozone chemistry and technology. Advances in Chemistry Series 21. p. 398-404. Washington, American Chemical Society, 1959.

78. Griggs, M., J. Chem. Phys. 49, no. 2:857-9(July 15, 1968).

79. Green, J. W. Personal communication, 1970.

80. Spurry, Z., Talanta 9:885-9(1962).

81. Ashmore, P. G., Parker, A. J., and Stearne, D. E., Trans. Faraday Soc. 67, no. 586, Part 10:3081-93(Oct., 1971).

82. Porter, G., and Wright, F. J., Disc. Faraday Soc. 14:23-34(1953).

83. Pierce, W. C., Haenisch, E. L., and Sawyer, D. T. Quantitative analysis. 4th ed. New York, John Wiley and Sons, Inc., 1958. 497 p.

84. Chen, T., Anal. Chem. 39, no. 7:804-13(1967).

85. Institute Technique 5, 1951.

86. Institute Method 112, 1951.

87. Trautwein, N. L., and Guyon, J. C., Anal. Chem. 40, no. 3:639-41(1968).

88. Reid, R. C., and Sherwood, T. K. The properties of gases and liquids. New York, McGraw-Hill, 1958. 386 p.

89. Mathews, J. F., Chem. Rev. 72, no. 1:71-100(Feb., 1972).

90. Herron, J. T., J. Phys. Chem. 67, no. 12:2864-5(Dec. 16, 1963).

APPENDIX I

COATING OF COOLING COIL AND OTHER METALS WITH EPOXY

The epoxy was supplied free of charge by Reichhold Chemicals, Inc. After the parts were thoroughly cleaned they were coated in the following manner. Liquid Epoxy Resin 37-140 was mixed with Polyamide Hardener 37-612 in a ratio of 10 parts 37-140 to 6 parts 37-612 by weight. The mixture was allowed to stand for at least 30 min. The viscosity was adjusted as desired with xylene. The epoxy mixture was applied by dipping or with a paint brush. The coated part was allowed to stand for 30 min. to let solvent evaporate. The part was heated at 108°C. for 30 min. to achieve accelerated aging. The coating process was repeated if a thicker film was required. The pot life of the epoxy was 24 hours so that accelerated aging was useful in putting on several coats of epoxy.

APPENDIX II

PREPARATION OF THE TEMPERATURE BATH

As mentioned previously the temperature bath was a 2.5-gal. fish tank. This was first modified by building double windows into the ends. These served two purposes, insulation and prevention of fogging of the window. The windows were needed to allow passage of the activating light beam through the temperature bath and through the reactor body which was positioned in the light beam. The placement of the windows is shown in Fig. 16.

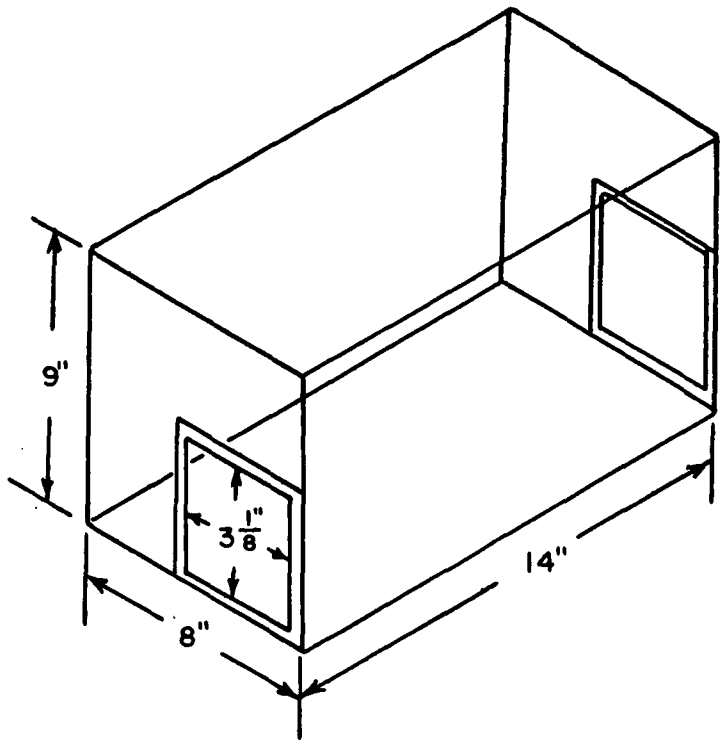

Figure 16. Position of Double Windows

The double windows were constructed in the following manner: A Plexiglas frame was fabricated to which a flat pyrex plate, 3 1/8-in. square, could be attached. The Plexiglas frame was then attached to the outside wall of the

temperature bath in the proper position. The space between the glass was filled with dry air and sealed. These windows functioned well with no internal fogging due to moisture. However, there was some fogging of the outside surface of the window. This fogging was prevented by forcing a stream of air over the surface. To the rest of the outside glass surface of the reactor was attached special optical black paper. Polystyrene foam of thickness 0.5 to 1.0 in. was placed over the paper to act as insulation.

APPENDIX III

CHANGE IN TRANSMITTANCE DUE TO CHANGES IN CONCENTRATION OF ETHYLENE GLYCOL-WATER SOLUTIONS

Table XXII presents the effect on transmission of light of wavelength 365 nm. through solutions of various concentrations of ethylene glycol and water.

TABLE XXII

TRANSMISSION CHANGES IN ETHYLENE GLYCOL-WATER SOLUTIONS OF LIGHT OF 365 NM. WAVELENGTH

Ethylene Glycol, % by volume	Transmittance of 365 nm. Light vs. H_2O in Reference Beam
0	100.0
10	100.1
20	100.2
30	100.3
40	100.4
50	100.5
60	100.6
70	100.6
80	100.7
90	100.8
100	100.9

APPENDIX IV

SPECIFIC GRAVITY VERSUS TEMPERATURE FOR ETHYLENE GLYCOL-WATER SOLUTIONS

Table XXIII is prepared from data found in Reference (71); Table 3.9, page 40 and Fig. 3.7, page 41.

TABLE XXIII

SPECIFIC GRAVITY VERSUS TEMPERATURE OF AN ETHYLENE GLYCOL-WATER SOLUTION 40% BY VOLUME ETHYLENE GLYCOL

Temperature, °C.	Specific Gravity, t/60°F.
-1.0	1.065
4.4	1.063
10.0	1.060
15.4	1.058
21.2	1.055
26.8	1.052
32.2	1.048

APPENDIX V

CALIBRATION OF THE PRESSURE MEASUREMENT APPARATUS AND DETERMINATION OF REACTOR PRESSURE

To calibrate the pressure measurement apparatus, the atmospheric pressure in mm. Hg was first recorded. With the reactor at atmospheric pressure and the potentiometer of the transducer indicator at zero, the zero knob was adjusted so that there was zero meter deflection at meter sensitivities of 100, 30, and 10. The reactor was partially evacuated and the pressure inside the reactor determined by a mercury manometer in conjunction with a cathetometer. The value obtained when the pressure inside the reactor was divided by the atmospheric pressure was placed on the potentiometer of the transducer indicator. The span knob of the transducer indicator was adjusted so that there was zero meter deflection at meter sensitivities of 100, 30, and 10. The process was repeated until there was no further adjustment of the zero and span knobs. A full-scale reading now corresponds to the atmospheric pressure at the time of calibration.

To obtain pressure readings, the atmospheric pressure was first recorded. The potentiometer was adjusted so that there was zero deflection of the meter at 100, 30, and 10 sensitivities. The pressure inside of the reactor was calculated from the following equation:

$$\begin{pmatrix}\text{Pressure}\\ \text{in}\\ \text{Reactor}\end{pmatrix} = \begin{pmatrix}\text{Atmospheric Pressure}\\ \text{at Time of}\\ \text{Reading}\end{pmatrix} - \begin{pmatrix}\text{Atmospheric Pressure}\\ \text{at Time of}\\ \text{Calibration}\end{pmatrix}\left(\frac{\text{Potentiometer Reading}}{100}\right).$$

APPENDIX VI

PROCEDURE, OPERATING CONDITIONS, AND SAFETY PRECAUTIONS FOR GENERATION OF OZONE

Foreign gases were removed from the ozonizer by alternately filling the ozonizer with oxygen and evacuating. This procedure was followed four times. The three-way stopcock was closed so that the manometer was still in the system. Oxygen was introduced to the ozonizer through the two-way stopcock. The ozonizer was filled to approximately 15 p.s.i.g. with oxygen at room temperature. The ozonizer body was then gradually immersed in liquid nitrogen. When the H_2SO_4 manometer has stopped dropping, the oxygen has reached the proper temperature and has liquified with a vapor pressure of 162 mm. Hg. This gave enough oxygen in the ozonizer to produce more than 5.6×10^{-3} moles of ozone which was used in most experimental runs; however, when runs requiring more ozone were made, additional oxygen was added by opening briefly the two-way stopcock while the ozonizer body was still immersed in liquid nitrogen. The level of liquid nitrogen was above the top of the electrodes before generation of ozone was initiated. After the oxygen was added and cooled and care had been taken to fully immerse the electrodes in liquid nitrogen, the door of the hood in which the ozonizer was mounted was pulled down as far as possible. The electrical circuit was turned on and the variac setting moved from zero until the voltmeter in the primary circuit registered 90 volts. The current at this time was approximately 0.14 amp. It took approximately one hour for all of the oxygen to be converted to ozone unless extra oxygen was added. Complete conversion of the oxygen to ozone was indicated by a difference of the H_2SO_4 manometer of less than 25 mm. If after one hour the H_2SO_4 manometer had not reached a difference of 25 mm., the excess oxygen was pumped off by means

of the vacuum pump while the ozonizer was still immersed in liquid nitrogen and the electrical circuit turned off. Once a sufficient amount of ozone was produced, the electrical circuit was turned off by reversing the start-up procedure. The next step was to evaporate the ozone. This was done by gradually lowering the dewar until the ozone started to evaporate as indicated by an increase in pressure on the H_2SO_4 manometer. A slow rate of evaporation was desired since explosion might occur if the rate was too great. Once the ozone was evaporated and confined to the ozonizer it was ready to be introduced into the reactor.

APPENDIX VII

THEORY, PREPARATION, AND USE OF THE POTASSIUM FERRIOXALATE ACTINOMETER

Except for a few specific situations where comments are made about the system under study, the following can be found in more detail in (75,76,8).

THEORY

When sulfuric acid solutions of potassium ferrioxalate, $K_3Fe(C_2O_4)_3$, are irradiated by light of wavelength 250 to 577 nm., a simultaneous reduction of iron to the ferrous state and oxidation of oxalate occur. The quantum yields of Fe^{2+} formation have been accurately determined for the range 480 to 253.7 nm. To determine the amount of Fe^{2+} formed, it is complexed with 1,10-phenanthroline and the absorption of this complex measured.

PREPARATION

Potassium ferrioxalate was prepared in the following manner: 1.5M solutions of potassium oxalate, A.R., and ferric chloride, A.R., were prepared. To 1000 ml. of 1.5M potassium oxalate was added 333 ml. of 1.5M ferric chloride with vigorous stirring in the dark. The precipitated $K_3Fe(C_2O_4)_3$ was recrystallized, three times, from warm water and dried. The crystals were stored in a covered container in the dark.

For use in chemical actinometry, a 0.006M solution of $K_3Fe(C_2O_4)_3$ in 0.1N H_2SO_4 was prepared by dissolving 2.947 grams of the solid in 800 ml. of H_2O, addition of 100 ml. of 1.0N H_2SO_4, and dilution to 1000 ml. by H_2O. This solution was then stored in a brown bottle in the dark.

It was necessary that all manipulation of potassium ferrioxalate, crystals and solution, be done in the dark. Therefore, the laboratory in which the work was performed was blacked out and work was carried out using a red photographic safelight.

USE

CALIBRATION CURVE

A calibration curve for analyses of Fe^{2+} complex was prepared using the D.U. spectrophotometer located in Room 102-A. The following procedure was used to establish the calibration curve. Approximately 0.1N potassium permanganate was prepared and standardized with arsenic trioxide according to procedures given in (83). A solution approximately 0.1M $FeSO_4$ and 0.1N H_2SO_4 was prepared by dissolving 14 grams of $FeSO_4 \cdot 7H_2O$ in a 500-ml. volumetric flask, addition of 50 ml. of 1.0N H_2SO_4 and dilution to 500 ml. with H_2O. The $FeSO_4$ solution was standardized using the potassium permanganate: 10 ml. of $FeSO_4$ solution was placed in a 250-ml. Erlenmeyer flask and diluted to 100 ml. with H_2O, 4 drops of 85% phosphoric acid was added, the mixture was titrated dropwise by potassium permanganate to a faint pink end point. Solutions were prepared to be read on the D.U. spectrophotometer: 2 ml. of standardized $FeSO_4$ solution were diluted with 0.1N H_2SO_4 in a 500-ml. volumetric flask, to 25-ml. volumetric flasks add 0, 0.5, 1.0,...,5.0, 5.5 ml. of this freshly prepared $FeSO_4$ solution, and sufficient 0.1N H_2SO_4 to give a total liquid volume of 10 ml., add 2 ml. of 0.1% 1,10-phenanthroline solution (1.0008 grams of O-phenanthroline, reagent A.C.S., diluted to 1 liter) and shake, add 5 ml. of buffer solution (600 ml. of 1N $NaC_2H_3O_2$ and 360 ml. of 1N H_2SO_4 diluted to 1 liter with H_2O) and shake, dilute to volume with H_2O, let color develop for 1.5 hours in dark. Read solutions in 1-cm. silica cells at 510 nm. versus H_2O in reference beam.

The above procedure was followed on three separate days. The data obtained are given in Table XXIV. A linear regression using all the points of the three sets was made and plotted in Fig. 17. The slope, 1.101×10^4 liter/mole-cm., compares favorably with one given by Calvert and Pitts (8) of 1.11×10^4. The y-intercept of -0.0001 was considered to be zero. On April 18, 1971 a check of the curve was made; these points are shown in Table XXIV and Fig. 17 and compare favorably with the original data.

TABLE XXIV

DATA USED FOR ESTABLISHMENT OF CALIBRATION CURVE FOR Fe^{2+} COMPLEX

Date of Attainment of Data	Absorbance Minus Blank at 510 nm.	Moles of Fe^{2+} x 10^6/liter
10/28/68	0.185	17.01
	0.282	25.51
	0.373	34.02
	0.470	42.52
	0.561	51.02
	0.656	59.53
	0.752	68.03
	0.849	76.54
10/29/68	0.188	16.98
	0.281	25.46
	0.371	33.95
	0.466	42.44
	0.557	50.93
	0.650	59.42
	0.748	67.90
	0.842	76.39
11/5/68	0.188	16.78
	0.278	25.19
	0.369	33.57
	0.463	41.96
	0.552	50.35
	0.642	58.74
	0.739	67.14
	0.827	75.53
4/18/71[a]	0.376	34.27
	0.750	68.54

[a] Data used to check calibration curve.

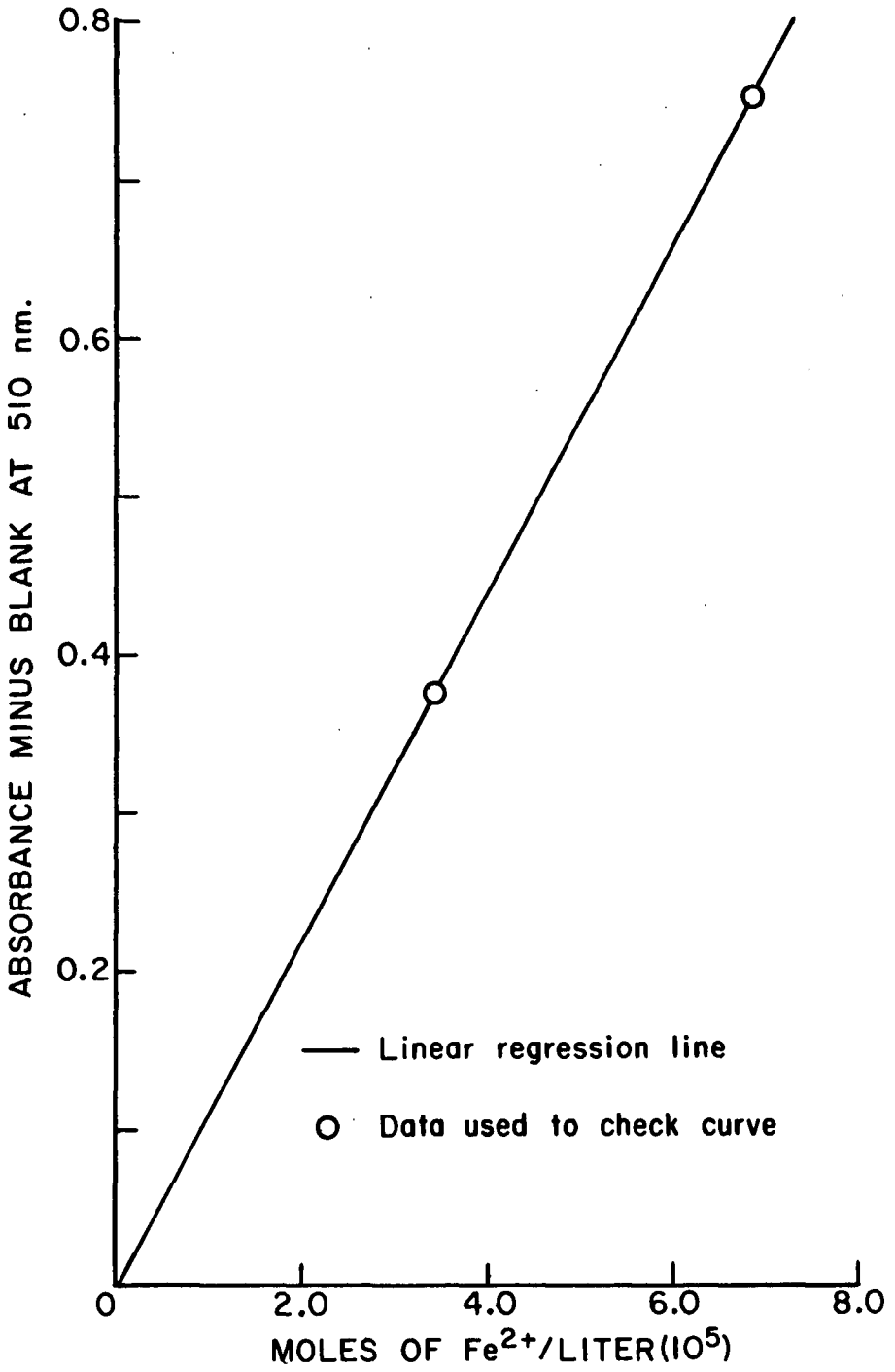

Figure 17. Calibration Curve for Fe^{2+}

DETERMINATION OF LIGHT INTENSITY

To determine light intensity, a known volume of the 0.006M $K_3Fe(C_2O_4)_3$ solution was irradiated for a known time. The irradiated solution was then mixed thoroughly and an aliquot taken and placed in a 25-ml. volumetric flask; the rest of the procedure was identical with that used to prepare the calibration curve. After the absorbance was read and corrected for a blank prepared with unirradiated actinometer solution the concentration of Fe^{2+} moles/liter was calculated from the equation,

$$x = \frac{y + 0.0001}{1.101\ (10^4)}\ , \tag{137}$$

where y is the corrected absorbance, 0.0001 is the intercept of the linear regression, and 1.101 (10^4) liter/mole-cm. is the slope of the linear regression. The number of Fe^{2+} ions formed during the photolysis ($\eta_{Fe^{2+}}$) was then calculated from,

$$\eta_{Fe^{2+}} = \frac{6.023\ (10^{20})\ V_1 V_3 x}{V_2}\ , \tag{138}$$

where V_1 = the volume of actinometer solution irradiated, ml.;

V_2 = the volume of aliquot taken for analysis, ml.; and

V_3 = the final volume to which the aliquot V_2 is diluted, ml.

The light intensity was then calculated from the following:

$$I_o = \frac{\eta_{Fe^{2+}}}{\phi_{Fe^{2+}}\ t}\ , \tag{139}$$

where $\phi_{Fe^{2+}}$ = the quantum yield for 0.006M $K_3Fe(C_2O_4)_3$ at 366.0 nm. and equals 1.26 molecules/quanta; and

$\underline{t}$ = time of exposure.

For determination of light intensity in the system studied, a cell was prepared that held 100 ml. of solution. The cell was fabricated from the bottom of a 400-ml. beaker, a piece of 1.5-cm. pyrex tubing and a pyrex plate 8.0-cm. square and 2 mm. in thickness. The tubing was fused to the bottom of the beaker by a suck seal. The beaker was cut 2.7 cm. from the bottom and the cut smoothed by grinding with No. 600 carborundum and water on a flat plate. The pyrex plate was cemented to the smoothed surface with epoxy cement. The assembled actinometer cell is shown in Fig. 18.

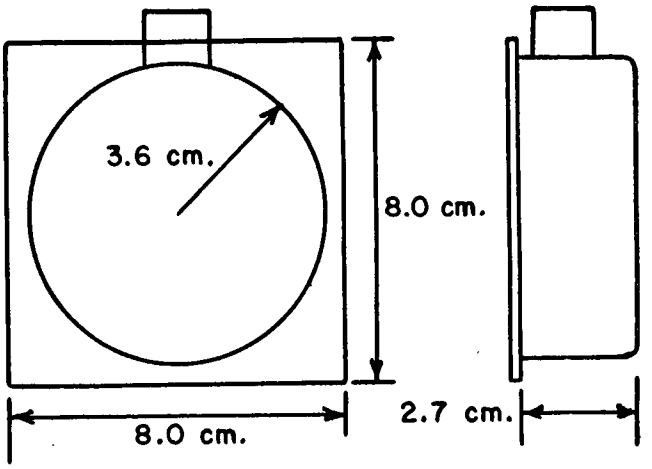

Figure 18. The Assembled Actinometer Cell

A holder was made for the cell which assured consistent placement of the cell at the plane of measurement. Calvert and Pitts (8) indicate that a path length of only 1.5 cm. is needed for complete absorption of light of wavelength 365-366.5 nm. by 0.006M $K_3Fe(C_2O_4)_3$.

APPENDIX VIII

PURIFICATION AND STORAGE OF CCl_4

Because the carbon tetrachloride came into contact with the reactants and products it was imperative that it was free of any impurities which would react with these species. Analytical reagent-grade carbon tetrachloride was first saturated with chlorine and allowed to sit overnight. It was washed with aqueous NaOH to remove the chlorine, and rinsed repeatedly with water until no residual NaOH was evident. The carbon tetrachloride was dried using A.R. calcium chloride. The dried carbon tetrachloride was distilled at a dropwise rate. The first portion to come over was stored for later recycling. The freshly distilled carbon tetrachloride was stored under nitrogen in a glass bottle.

Each experimental run required 250 ml. of carbon tetrachloride. After it was extracted with water to obtain the products, the carbon tetrachloride was saved for recycling. When a sufficient amount of carbon tetrachloride was obtained for recycling this material was purified as before but the chlorine saturation procedure was eliminated. Periodically, additional fresh A.R. carbon tetrachloride was added to the carbon tetrachloride to be recycled without chlorine saturation.

The purification procedure was found in Reference (80).

APPENDIX IX

PROCEDURES AND CALIBRATION CURVES FOR ANALYTICAL PROCEDURES

TEST A. DETERMINATION OF HYPOCHLORITE

The procedure used for the determination of hypochlorite was taken directly from Chen (84). One ml. of a freshly prepared 0.2 gram KI/ml. solution was placed in a 50-ml. volumetric flask. The stem of the flask was flushed with H_2O. Five ml. of 0.035M $NaHCO_3$ were added and the stem again flushed with H_2O. Up to 2.0 (10^{-6}) equiv. of ClO^- were added. The flask was filled to the mark with H_2O and the contents mixed thoroughly. The absorbance was measured vs. H_2O at 287 nm. in 1-cm. silica cells. The reading was corrected according to a reagent blank read at the same wavelength. All unknown samples were run in duplicate and the average used in determination of concentration.

A calibration curve was prepared in the following manner: iodine solution was prepared and standardized using arsenious oxide as described in (83). Thiosulfate solution was prepared from standard volumetric solution and standardized using iodine solution as described in (83). Arsenious oxide solution was prepared as in (83) and standardized according to Institute Technique 5 (85). A solution of hypochlorite and chlorite containing approximately 0.16N hypochlorite was prepared from Hi-lex Bleach (Hilex Company, Minneapolis, Minn.) and standardized using Institute Method 112 (86). One ml. of the standardized hypochlorite solution was diluted to 500 ml. in a volumetric flask. One, 1.5, 2.0, 2.5, 3.0, 4.0,....,7.0 ml. of this solution was added to 50-ml. volumetric flasks already containing $NaHCO_3$ and KI and the previous procedure was continued. A calibration curve was obtained by plotting the corrected absorbance versus the

total equivalents of ClO^- placed in the flask. The data used for the calibration curve are given in Table XXV. The calibration curve is shown in Fig. 19. A linear regression of the data gave a y-intercept of -0.0319 and a slope of 0.361 (10^6). A check of the calibration curve was made on April 16, 1971 and these data are included in Table XXV and Fig. 19.

TABLE XXV

DATA USED TO ESTABLISH A CALIBRATION CURVE FOR TEST A, DETERMINATION OF ClO^-

Date Data Attained	Absorbance Minus Blank at 287 nm.	Equivalents of ClO^- x 10^6
1/28/70	0.166	0.5547
	0.222	0.7396
	0.296	0.9245
	0.365	1.109
	0.499	1.479
	0.629	1.849
	0.769	2.219
1/28/70	0.174	0.5547
	0.238	0.7396
	0.307	0.9245
	0.376	1.109
	0.509	1.479
	0.640	1.849
	0.770	2.219
1/31/70[a]	0.170	0.5556
	0.234	0.7408
	0.305	0.9260
	0.371	1.111
	0.509	1.482
	0.636	1.852
	0.770	2.222
4/16/71[b]	0.893	2.516

[a] To each of these samples was added 1 ml. of 0.6971 g./liter $KClO_4$; this showed no effect on the method by addition of excess ClO_4^-.

[b] Data used to check calibration curve.

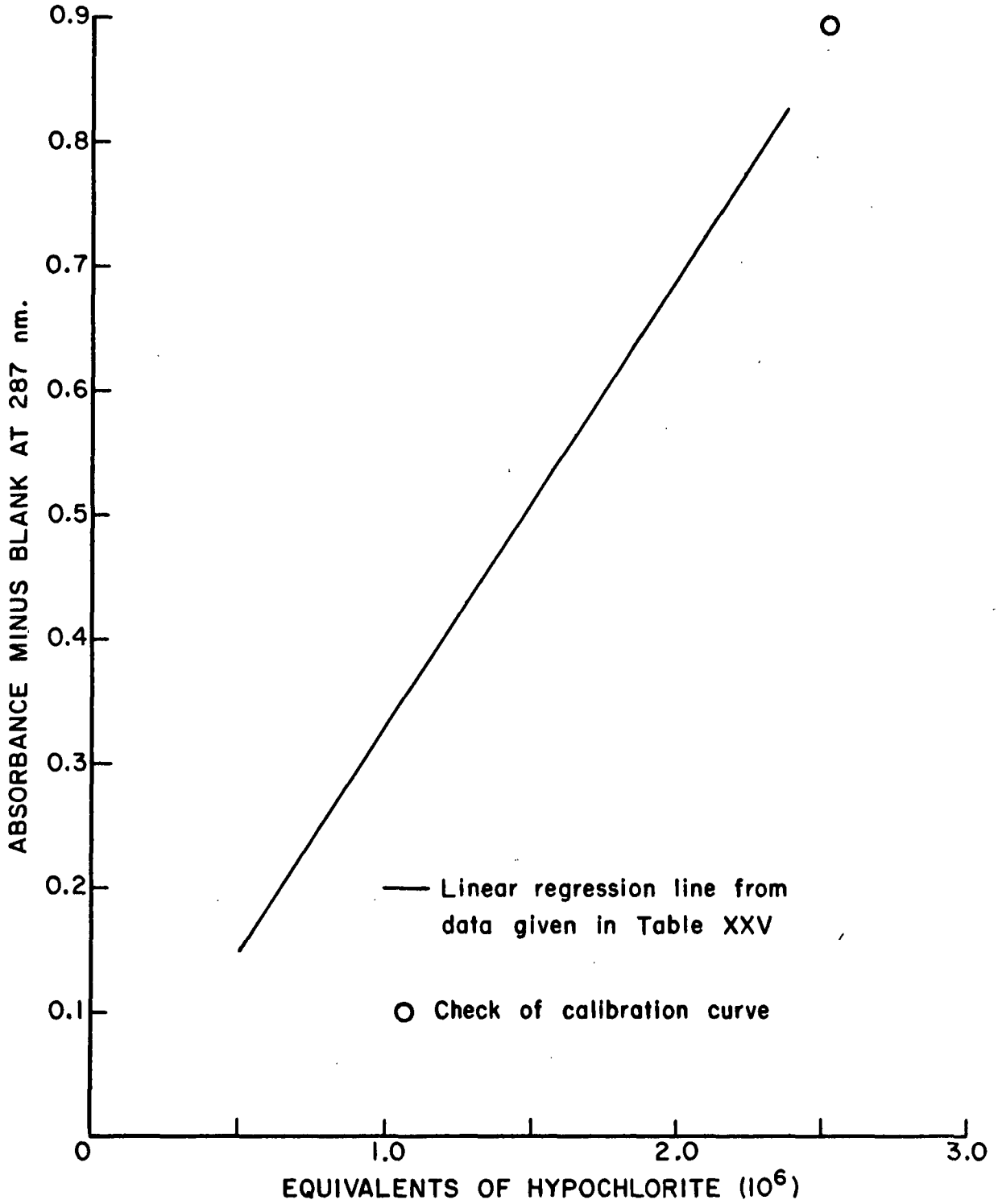

Figure 19. Calibration Curve for Test A, Determination of ClO^-

TEST B. DETERMINATION OF TOTAL HYPOCHLORITE AND CHLORITE

The procedure used for the determination of total hypochlorite and chlorite was taken directly from Chen (84). One ml. of a freshly prepared 0.2 gram KI/ml. solution was placed in a 50-ml. volumetric flask. The stem of the flask was flushed with H_2O. Up to 2.3×10^{-6} equivalents of hypochlorite and chlorite were added and flushed in with H_2O. This was diluted to approximately 45 ml. with H_2O and 0.4 ml. of 1.0N H_2SO_4 added. The flask was filled to the mark with H_2O and the contents mixed thoroughly. The absorbance was measured versus H_2O at 287 nm. in a 1-cm. silica cell. The reading was corrected according to a reagent blank read at the same wavelength. Duplicates were run on all unknown samples.

A calibration curve was prepared in the following manner: a hypochlorite-chlorite solution was standardized by Institute Method 112 (86), as in the procedure for Test A. One ml. of the standardized solution was diluted to 500 ml. and this diluted solution was used as the source of hypochlorite and chlorite in the above procedure. One, 1.5, 2.0, 2.5, 3.0, 4.0, ...,7.0 ml. of this material was used. A calibration curve was obtained by plotting the corrected absorbance versus the total equivalents of ClO^- and ClO_2^- placed in the flask. The data used for the calibration curve are given in Table XXVI. A linear regression of the data gave a y-intercept of -0.0103 and a slope of 0.365×10^6, a plot of which is given in Fig. 20. A check of the calibration curve was made on April 13, 1971 and these data are included in Table XXVI and Fig. 20.

TABLE XXVI

DATA USED TO ESTABLISH A CALIBRATION CURVE FOR TEST B, DETERMINATION OF TOTAL HYPOCHLORITE AND CHLORITE

Date Data Attained	Absorbance Minus Blank at 287 nm.	Equivalents of ClO^- and ClO_2^- x 10^6
1/26/70	0.201	0.5592
	0.258	0.7456
	0.329	0.932
	0.397	1.118
	0.545	1.491
	0.678	1.864
	0.819	2.237
1/26/70	0.197	0.5592
	0.255	0.7456
	0.333	0.932
	0.403	1.118
	0.531	1.491
	0.659	1.864
	0.808	2.237
1/31/70[a]	0.197	0.5583
	0.257	0.7444
	0.329	0.9305
	0.398	1.117
	0.529	1.489
	0.663	1.861
	0.801	2.233
4/13/71[b]	0.181	0.5068
	0.366	1.014
	0.544	1.521
	0.737	2.027

[a]To each of these samples was added 1 ml. of 0.6971 g./liter $KClO_4$; this showed no effect on the method by addition of excess ClO_4^-.

[b]Data used to check calibration curve.

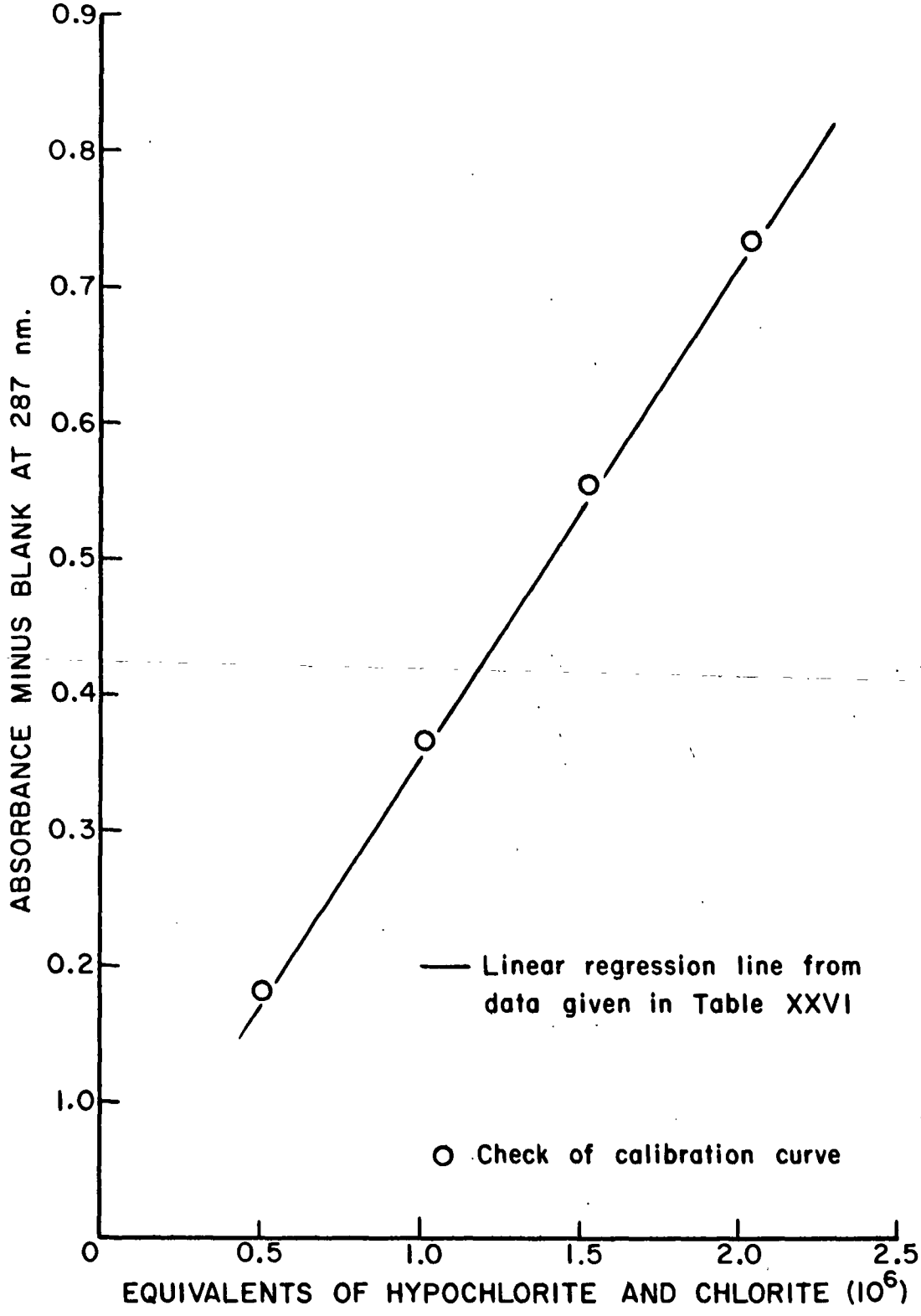

Figure 20. Calibration Curve for Test B, Determination of Total Hypochlorite and Chlorite

TEST C. DETERMINATION OF TOTAL CHLORITE AND CHLORATE

The procedure used for the determination of total chlorite and chlorate is a modified form of that given by Chen (84). To a 10-ml. volumetric flask up to 3.0×10^{-6} equivalents of chlorite and chlorate were added. The stem was rinsed with H_2O so that total volume of liquid in the flask was 4.5 ml. Added to this was 0.3 ml. of 0.05N NaOH and 0.1 ml. of freshly prepared 0.088N H_2O_2 (1 ml. of 30% H_2O_2 diluted to 100 ml.). The flask was placed in a boiling water bath for 15 min. Added to this was 0.1 ml. of 0.001M $CuSO_4$ and the flask was kept in the boiling water bath for 15 more minutes. The flask was placed in an ice-water bath. Three ml. of concentrated H_2SO_4 were added and mixed carefully to try to prevent generation of excess heat. One ml. of freshly prepared 0.02 g. $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$/ml. solution was added and the solution was diluted to the mark with H_2O and mixed. This stood for 15 min. and the absorbance was measured *versus* H_2O at 301 nm. in 1-cm. silica cells. The reading was corrected according to a reagent blank *versus* H_2O. Duplicates were run on unknowns. The addition of 0.05N NaOH, 0.088N H_2O_2, and 0.001M $CuSO_4$ were the modifications to the procedure of Chen (84). The addition of 0.05N NaOH and 0.088N H_2O_2 and the subsequent boiling destroyed any hypochlorite in the solution. The addition of 0.001M $CuSO_4$ and subsequent boiling insured breakdown of all of the H_2O_2. Both hypochlorite and H_2O_2 gave a positive test for chlorite and chlorate; this is why they had to be destroyed.

A calibration curve was prepared in the following manner: standard solutions of $KClO_3$ were prepared by first drying A.R. $KClO_3$ in an oven at 106°C. for two hours. The dried $KClO_3$ was then weighed and the weighed material dissolved in water in a volumetric flask. Two $KClO_3$ solutions were prepared in this manner, one 4.57×10^{-7} moles $KClO_3$/ml. and the other 4.30×10^{-7} moles

$KClO_3$/ml. The equivalents of ClO_3^- were calculated on the basis of 6 equivalents per mole. These solutions were then used as the source of chlorate in the above procedure. A calibration curve was obtained by plotting the corrected absorbance versus total equivalents of ClO_3^- placed in the flask. The data used for the calibration curve are given in Table XXVII. A linear regression of the data gave a y-intercept of -0.0281 and a slope of 0.277×10^6, a plot of which is given in Fig. 21. A check of the calibration curve was made several times. The data obtained by checks of March 30, 1970 and April 16, 1971 are given in Table XXVII and Fig. 21.

TABLE XXVII

DATA USED TO ESTABLISH A CALIBRATION CURVE FOR TEST C, DETERMINATION OF TOTAL CHLORITE AND CHLORATE

Date Data Attained	Absorbance Minus Blank at 301 nm.	Equivalents of ClO_2^- and ClO_3^- x 10^6
1/17/70	0.355	1.371
	0.581	2.194
1/20/70	0.194	0.774
	0.257	1.032
	0.318	1.29
	0.405	1.548
	0.541	2.064
	0.703	2.58
1/21/70	0.187	0.774
	0.265	1.032
	0.325	1.29
	0.393	1.548
	0.531	2.064
	0.673	2.58
1/21/70	0.193	0.774
	0.265	1.032
	0.319	1.29
	0.398	1.548
	0.534	2.064
	0.690	2.58
1/22/70	0.204	0.8226
	0.282	1.097
	0.345	1.371

TABLE XXVII (Continued)

DATA USED TO ESTABLISH A CALIBRATION CURVE FOR TEST C, DETERMINATION OF TOTAL CHLORITE AND CHLORATE

Date Data Attained	Absorbance Minus Blank at 301 nm.	Equivalents of ClO_2^- and ClO_3^- x 10^6
1/22/70	0.430	1.645
	0.572	2.194
	0.739	2.742
1/22/70	0.194	0.8226
	0.277	1.097
	0.347	1.371
	0.411	1.645
	0.548	2.194
	0.737	2.742
1/30/70[a]	0.195	0.774
	0.260	1.032
	0.325	1.29
	0.386	1.548
	0.535	2.064
	0.696	2.58
1/30/70[a]	0.202	0.8226
	0.282	1.097
	0.354	1.371
	0.426	1.645
	0.583	2.194
	0.734	2.742
3/20/70	0.256	1.032
	0.393	1.548
	0.544	2.064
	0.684	2.58
3/30/70[b]	0.249	1.032
	0.395	1.548
	0.541	2.064
4/16/71[b]	0.362	1.371

[a] To each of these samples was added 1 ml. of 0.6971 g./liter $KClO_3$; this showed no effect on the method by addition of excess ClO_4^-.

[b] Data used to check calibration curve.

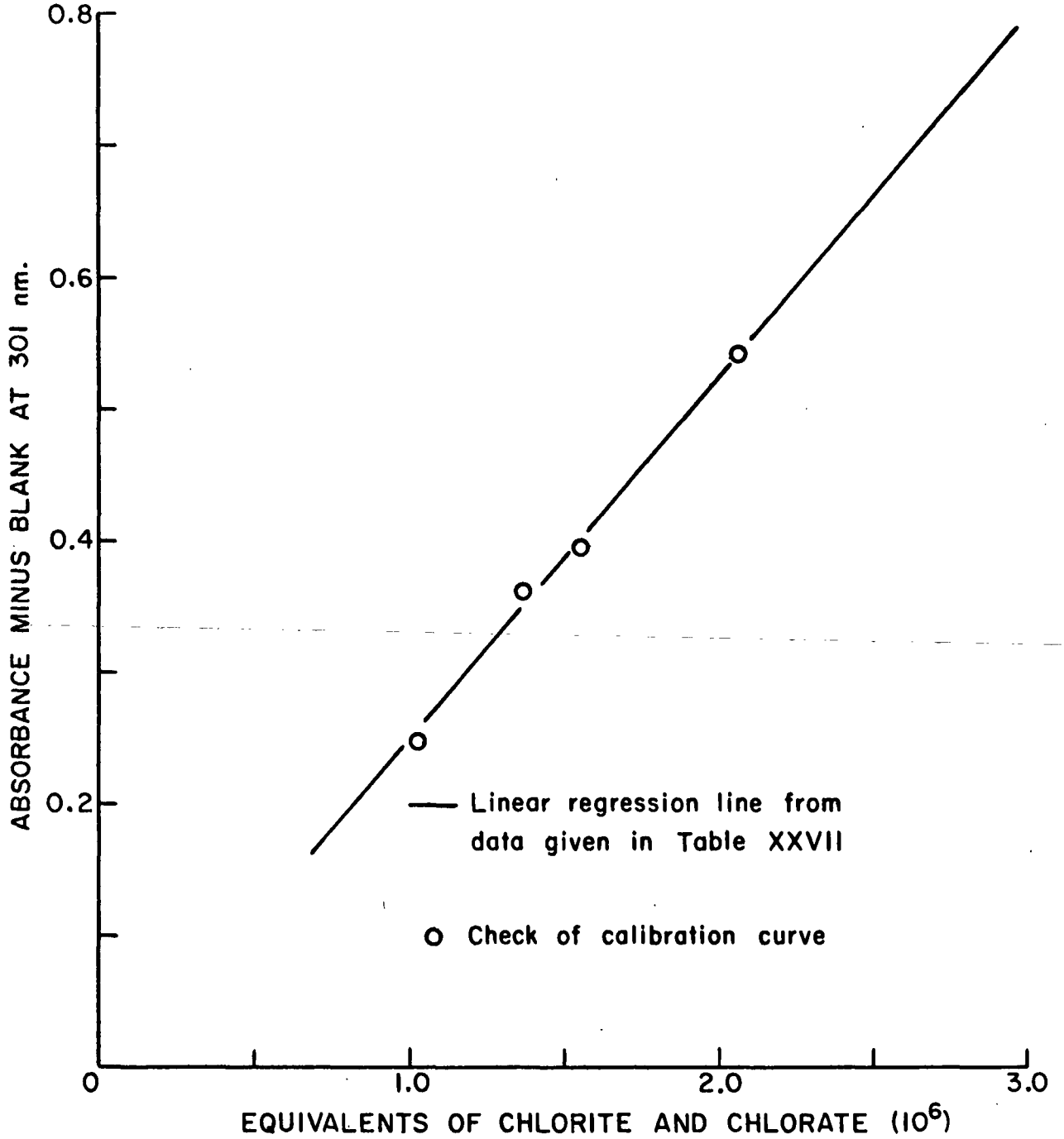

Figure 21. Calibration Curve for Test C, Determination of Total Chlorite and Chlorate

TEST D. DETERMINATION OF PERCHLORATE

The procedure used for the determination of perchlorate is a modified form of that given by Trautwein and Guyon (87). To a 50-ml. volumetric flask was added up to 4.5×10^{-6} moles of perchlorate. This was diluted to 5.0 ml. One ml. of concentrated HCl was added and the flask placed in a boiling H_2O bath for 15 min. (this treatment was the modification of the Trautwein and Guyon procedure; it effectively removed ClO^-, ClO_2^-, and ClO_3^-, all of which interfere in the test). The flask was cooled to room temperature with cold H_2O. Four ml. of aqueous 0.0950 g./liter potassium perrhenate, 3.0 ml. of 1:1 hydrochloric acid, 17.0 ml. of methanol, and 7.0 ml. of 8.5% Tin II chloride (freshly prepared from 10 g. of $SnCl_2$, dissolved in 10.0 ml. of concd. HCl, and diluted to 100 ml. with H_2O) were added. This was mixed and placed in a water bath at 55°C. ± 5° for 45 min. Without cooling, 5.00 ml. of α-furildioxime solution (7.000 g. of α-furildioxime dissolved in methanol and diluted to 1 liter) were added. This was mixed and placed in a 55°C. ± 5° water bath for 30 min. and then placed in a 20°C. water bath for 15 min. The solutions were diluted to mark and the absorbance measured versus H_2O at 532 nm. in 1-cm. silica cells. The reading was corrected according to a reagent blank versus H_2O. In this test the blank gave the highest absorbance, with the perchlorate interfering with the development of the perrhenate, α-furildioxime color complex.

A single calibration curve is not useful for this test. It was found that the time periods and amount of reagents added in this test were very critical. Therefore, even with a standard solution of perchlorate it was difficult to get consistent results between runs of the analytical procedure. However, it was shown that over the range of perchlorate concentration to be tested the absorbance versus concentration curve was linear, Fig. 22. Therefore, in each

subsequent run of the analytical procedure two known points were established using a standard solution of perchlorate. The concentrations of unknown solutions were then determined using a straight line between these two known points. In all cases duplicates were run on each sample. One stipulation of the procedure was that the unknown point falls between the two known points. A second stipulation was that once the proper sample size is established for an unknown at least one more analytical test with duplicates has to be run on the unknown. The data listed in Table XXVIII illustrates the need for these stipulations.

TABLE XXVIII

VARIATIONS IN TEST D, DUE TO IMPROPER SAMPLE SIZE

Experimental Run	Date of Testing	Improper Sample Size, moles of ClO_4^- found x 10^6/ml.	Proper Sample Size, moles of ClO_4^- found x 10^6/ml.
R-34	8/22/71	--	0.725
	9/7/71	0.613	--
	9/8/71	0.425	--
	9/10/71	--	0.719
	9/11/71	--	0.756
	Average	0.519	Average 0.733
R-35	8/22/71	--	1.25
	9/7/71	--	1.065
	9/8/71	--	1.028
	9/10/71	--	1.10
	9/11/71	--	1.15
	Average		Average 1.118
R-36	9/4/71	0.488	--
	9/7/71	0.638	--
	9/8/71	0.550	--
	9/10/71	--	0.753
	9/11/71	0.610	0.796
	Average	0.572	Average 0.775
R-37	9/4/71	0.200	--
	9/7/71	0.410	--
	9/8/71	0.213	--
	9/10/71	--	0.560
	9/11/71	--	0.575
	Average	0.274	0.568

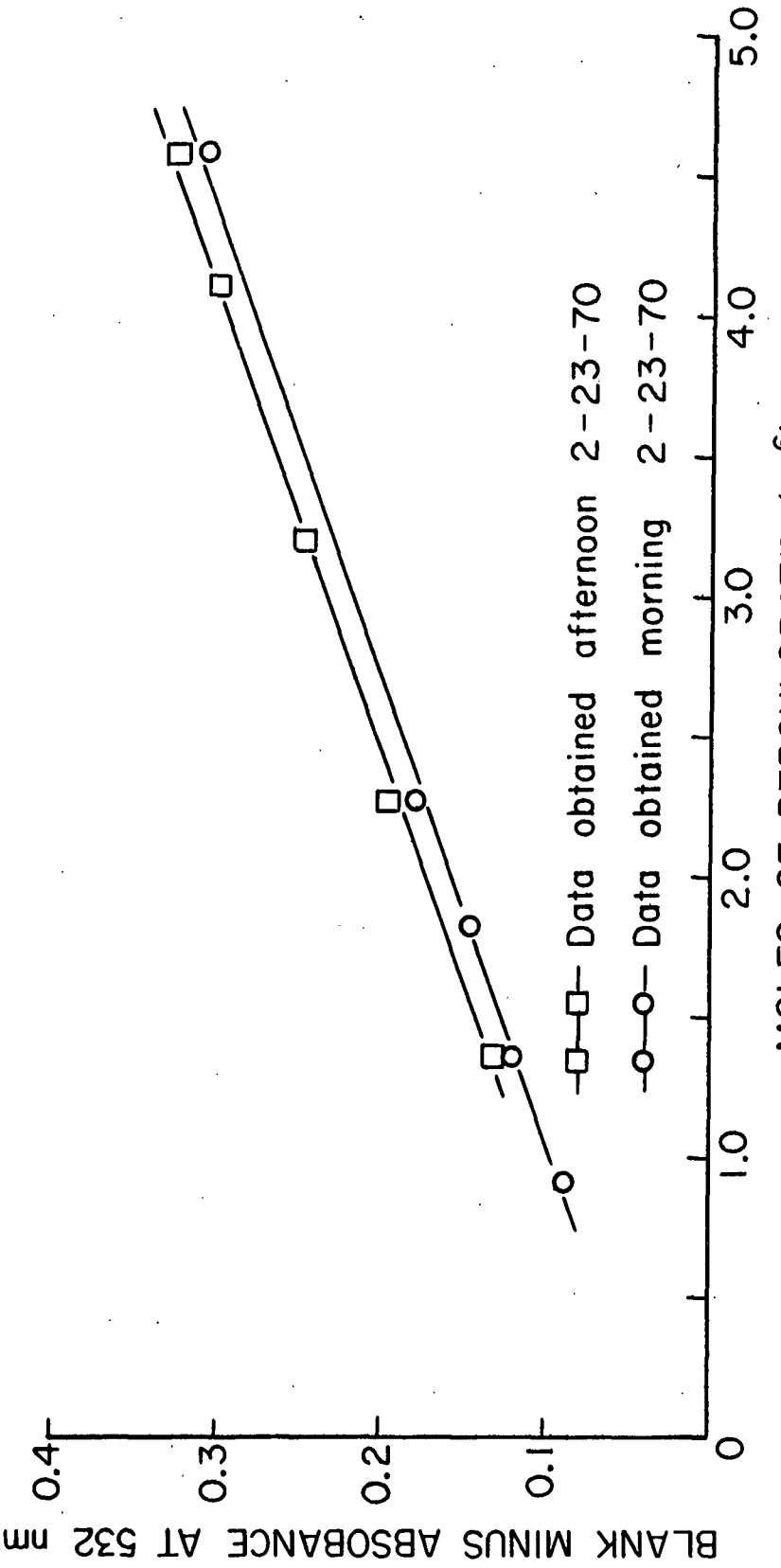

Figure 22. Linearity of Absorbance vs. Concentration Curve of Test D, Determination of Perchlorate

TEST E. DETERMINATION OF TOTAL CHLORIDE

The procedure used for the determination of total chloride was taken from Chen (84). The moles of Cl^- found represents total moles of ClO^-, ClO_2^-, and Cl^- present in the sample tested. Up to 2.5×10^{-6} moles of Cl^-, ClO^-, and ClO_2^- were placed in a 50-ml. volumetric flask and diluted to 10 ml. with H_2O. Then 5.0 ml. of 10^{-2}M arsenious oxide solution were added followed by 25 ml. of methyl cellosolve (ethylene glycol monomethyl ether, A.R.). The contents of the flask were mixed and 2.0 ml. of 0.02N H_2SO_4 added. After mixing, the flask was placed in a 50°C. water bath for 5.0 min. and then cooled to 20°C. in a water bath. Five ml. of 0.5N H_2SO_4 were then added and mixed. The solution was diluted to the mark with H_2O, mixed thoroughly, cooled to 20°C., and the volume adjusted again if necessary. The solution was then poured into a 125-ml. Erlenmeyer flask containing 0.100 gram of finely divided mercuric chloranilate. The mixture was swirled intermittently for 15 min. A portion of the mixture was placed in a centrifuge tube and centrifuged for 5 min. at 10,000 r.p.m. in a Beckman L-2 Ultracentrifuge, using rotor 30. The absorbance of the supernatant solution *versus* H_2O was then measured at 307 nm. in 1-cm. silica cells, and corrected for the reagent blank *versus* H_2O.

As in Test D, variation from test to test was found that prevented the attainment of a single calibration curve. Therefore, as in Test D, known samples were run along with the unknown samples. The straight line drawn between the known samples was then used to determine the unknowns. Three precautions had to be followed during each test to insure better accuracy: the mercuric chloranilate had to be finely divided, the time of contact of solution with mercuric chloranilate was critical (absorbance increases with time of contact), and temperature of solution in contact with mercuric chloranilate was critical

(absorbance increases as temperature increases for same time of contact). In each test up to 12 individual samples were run. The procedure followed was to make duplicates within each test. Therefore, two reagent blanks were made, their absorbance read and the average of the two absorbances was used as the absorbance of the reagent blank. Likewise, two individual samples at a known low chloride content (0.7×10^{-6} moles) and known high chloride content (1.75×10^{-6} moles) were made. Therefore, three unknowns, with duplicates, could be run during each test.

APPENDIX X

DETERMINATION OF CHLORINE MATERIAL BALANCE

In the use of Tests A through E for the determination of some chlorine species, certain procedures were followed to obtain the desired values. The tests gave the amount of species present in the sample size used in terms of equivalents or moles. The first step was to divide by the sample size to get the answer in terms of equivalents or moles per ml. Several tests accounted for two or three species. Since chlorite was assumed not to be present, Test A or B gave hypochlorite and Test C gave chlorate in terms of equivalents per ml. These were converted to moles by using 2 equivalents per mole for hypochlorite and 6 equivalents per mole for chlorate. Test D gave perchlorate in terms of moles, and Test E gave total hypochlorite, chlorite, and chloride in terms of moles. Once each species was converted to terms of moles per ml., the value was multiplied by the total volume of the sample to give total moles of each species in the sample. Table XXIX presents the data in this form. The estimations made are based on those discussed in the text.

TABLE XXIX

DATA USED FOR CHLORINE MASS BALANCE

		Species, moles x 10^3						Moles Cl Added x 10^3	% Recovered
Run	Sample	ClO^-	ClO_2^-	ClO_3^-	ClO_4^-	Cl^-	Total		
T-16-O_3	CCl_4-E	0.361	0.000	0.0009	0.000	(0.363)[a]	0.725		
	RR								
	0.1N NaOH	2.96		(0.050)		(3.06)	6.070		
							6.795	7.18	94.8
T-17-O_3	CCl_4-E	0.432	0.000	0.0019	0.000	(0.436)	0.870		
	RR								
	0.1N NaOH	2.06		(0.050)		(2.16)	4.270		
							5.140	5.66	90.9

TABLE XXIX (Continued)

DATA USED FOR CHLORINE MASS BALANCE

Run	Sample	Species, moles x 10^3						Moles Cl Added x 10^3	% Recovered
		ClO^-	ClO_2^-	ClO_3^-	ClO_4^-	Cl^-	Total		
T-18-O_3	CCl_4-E	0.278	0.000	0.0021	0.000	(0.282)	0.562		
	RR	0.005	0.000	0.0009	0.207	(0.007)	0.220		
	0.1N NaOH	2.36		(0.050)		(2.46)	4.870		
							5.652	5.58	101.3
T-19-O_3	CCl_4-E	0.351	0.000	0.0021	0.0412	(0.355)	0.749		
	RR	0.002	0.000	0.000	0.071	(0.002)	0.075		
	0.1N NaOH	2.33		(0.050)		(2.43)	4.810		
							5.634	5.90	95.4
T-20-O_3	CCl_4-E	0.460	0.000	0.002	0.126	(0.464)	1.052		
	RR	0.0100	0.000	0.0008	0.0325	(0.0116)	0.055		
	0.1N NaOH	1.80		(0.050)		(1.90)	3.750		
							4.857	5.50	88.4
T-21-O_3	CCl_4-E	0.441	0.000	0.0021	0.0915	(0.445)	0.980		
	RR	0.0179	0.000	0.0008	0.0638	(0.0195)	0.102		
	0.1N NaOH	4.18		(0.050)		(4.28)	8.510		
							9.592	10.14	94.6
T-22-O_3	CCl_4-E	0.371	0.000	0.000	0.000	(0.371)	0.742		
	RR	0.0233	0.000	0.0008	0.1063	(0.0249)	0.155		
	0.1N NaOH	5.04		(0.050)		(5.14)	10.230		
							11.097	11.18	99.3
T-23-O_3	CCl_4-E	0.424	0.000	0.0021	0.000	(0.428)	0.854		
	RR	0.0103	0.000	0.0008	0.0125	(0.0119)	0.036		
	0.1N NaOH	5.14		(0.050)		(5.24)	10.430		
							11.320	11.52	98.3
T-24-O_3	CCl_4-E	0.0813	0.000	0.0023	0.000	(0.0859)	0.170		
	RR	0.0010	0.000	0.0009	0.0205	(0.0028)	0.025		
	0.1N NaOH	0.206		(0.050)		(0.306)	0.562		
							0.757	0.758	99.9
T-25-O_3	CCl_4-E	0.392	0.000	0.000	0.000	(0.392)	0.784		
	RR	0.0029	0.000	0.000	0.0413	(0.0029)	0.047		
	0.1N NaOH	2.07		(0.050)		(2.17)	4.290		
							5.121	5.54	92.6
T-26-O_3	CCl_4-E	0.279	0.000	0.0021	0.000	(0.283)	0.564		
	RR	0.0067	0.000	0.000	0.070	(0.0067)	0.083		
	0.1N NaOH	2.22		(0.050)		(2.32)	4.590		
							5.237	5.47	95.8

TABLE XXIX (Continued)

DATA USED FOR CHLORINE MASS BALANCE

Run	Sample	Species, moles x 10^3						Moles Cl Added x 10^3	% Recovered
		ClO^-	ClO_2^-	ClO_3^-	ClO_4^-	Cl^-	Total		
T-27-O_3	CCl_4-E	0.349	0.000	0.0023	0.000	(0.354)	0.705		
	RR	0.0037	0.000	0.0004	0.113	(0.0045)	0.122		
	0.1N NaOH	2.15		(0.050)		(2.25)	4.450		
							5.277	5.55	95.2
T-28-O_3[b]	CCl_4-E	0.319	0.000	0.0045	0.000	0.401	0.725		
	RR	0.0068	0.000	0.000	0.010	0.0062	0.023		
	0.1N NaOH	2.18	0.000	0.041	0.000	2.34	4.561		
							5.309	5.61	94.7
T-28-O_3[c]	CCl_4-E	0.319	0.000	0.0045	0.000	(0.328)	0.652		
	RR	0.0068	0.000	0.000	0.010	(0.0068)	0.024		
	0.1N NaOH	2.18	0.000	(0.050)	0.000	(2.28)	4.510		
							5.186	5.61	92.7
R-1	CCl_4-E	0.627	0.000	0.0089	0.1312	(0.645)	1.412		
	RR	0.0032	0.000	0.0003	0.000	(0.0038)	0.007		
	0.1N NaOH	4.12	0.000	0.052	0.000	(4.224)	8.396		
							9.815	11.17	88.0
R-2	CCl_4-E	0.762	0.000	0.0123	0.1525	(0.7866)	1.723		
	RR	0.0052	0.000	0.0004	0.000	(0.0060)	0.012		
	0.1N NaOH	4.08	0.000	0.048	0.000	(4.176)	8.304		
							10.039	11.19	89.8
R-3	CCl_4-E	0.593	0.000	0.0051	0.050	(0.603)	1.251		
	RR	0.0042	0.000	0.0008	0.000	(0.0058)	0.011		
	0.1N NaOH	4.59	0.000	0.042	0.000	(4.674)	9.306		
							10.568	11.14	94.8
R-4	CCl_4-E	0.495	0.000	0.0047	0.000	(0.504)	1.004		
	RR	0.0039	0.000	0.0004	0.0538	(0.0047)	0.063		
	0.1N NaOH	4.87	0.000	0.079	0.000	(5.028)	9.977		
							11.044	11.17	99.0
R-5	CCl_4-E	0.627	0.000	0.0088	0.000	(0.6446)	1.280		
	RR	0.0201	0.000	0.0004	0.004	(0.0209)	0.045		
	0.1N NaOH	4.52	0.000	0.094	0.000	(4.708)	9.322		
							10.647	11.09	96.2
							Average % Cl Recovered		94.8

[a] Parentheses indicate estimated quantities.

[b] Mass balance obtained by complete analysis of T-28-O_3.

[c] Mass balance of T-28-O_3 obtained when estimations of Cl^- were made.

APPENDIX XI

DIFFUSION CALCULATIONS

CALCULATION OF DIFFUSION COEFFICIENTS OF ClO_2 THROUGH VARIOUS REACTION MIXTURES

Reid and Sherwood (88) give various methods for estimating diffusion coefficients in binary gas mixtures. The one used in the following calculations was

$$D_{12} = \frac{0.001858\ T^{3/2}\ [(M_1 + M_2)/M_1M_2]^{1/2}}{P\sigma_{12}^2\Omega_D}, \qquad (140)$$

where D_{12} = the diffusion coefficient of gas 1 through gas 2, $cm.^2 sec.^{-1}$;

T = the temperature, °K;

M_1 = the molecular weight of gas 1, $g.\ mole^{-1}$;

M_2 = the molecular weight of gas 2, $g.\ mole^{-1}$; and

P = total pressure, atm.

σ_{12} and Ω_D will be explained later; they are based on the Lennard-Jones Force Constants σ and ε of each gas.

For chlorine, He, and oxygen the Lennard-Jones Force Constants (Table XXX) were found in Table 8-2, page 270 of Reid and Sherwood (88). However, for ozone and chlorine dioxide these were not available and had to be estimated from critical constants through the empirical relations,

$$\frac{\varepsilon}{k} = 0.77\ T_c, \text{ and} \qquad (141)$$

$$\sigma = 0.833\ V_c^{1/3} \qquad (142)$$

given in (88). The critical constants for ozone are given by Mathews (89). Farrar (4) gave the critical temperature of chlorine dioxide as 426°K; and

due to similarities between chlorine dioxide and sulfur dioxide the V_c of chlorine dioxide was estimated to be 122 cm.^{3} g.-mole^{-1} (Table XXXI).

TABLE XXX

LENNARD-JONES FORCE CONSTANTS

Species	M, g. mole^{-1}	ε/k, °K	σ, A.
Cl_2	70.91	357.0	4.115
He	4.003	10.22	2.576
O_2	32.00	113.0	3.433
O_3	48.00	201.0	3.72
ClO_2	67.46	328.0	4.13

TABLE XXXI

CRITICAL CONSTANTS

Species	T_c, °K	P_c, atm.	V_c, cm.^{3} g.-mole^{-1}
O_3	261.0	55.0	89
SO_2	430.8	77.81	122
ClO_2	426.0	--	122

Using the following relationships,

$$\sigma_{12} = 1/2\ (\sigma_1 + \sigma_2), \tag{143}$$

$$\frac{\varepsilon_{12}}{k} = \sqrt{\frac{\varepsilon_1}{k} \cdot \frac{\varepsilon_2}{k}}, \tag{144}$$

and the relationship between $\frac{Tk}{\varepsilon}$ and Ω_D given in Table 8-1, page 269 of (88), Equation (140) was used to calculate PD_{12} for chlorine dioxide diffusing through chlorine, ozone, He, and oxygen (Table XXXII).

TABLE XXXII

$\underline{PD}_{12}$ OF ClO_2 DIFFUSING THROUGH VARIOUS GASES AT 273°K

$\underline{PD}_{12}$, $cm.^2 atm.sec.^{-1}$	Gases		σ_{12}	$\frac{\underline{kT}}{\underline{\varepsilon}_{12}}$	$\Omega_{\underline{D}}$
0.0494	ClO_2	Cl_2	4.12	0.798	1.612
0.0698	ClO_2	O_3	3.93	1.06	1.400
0.425	ClO_2	He	3.35	4.71	0.853
0.0967	ClO_2	O_2	3.78	1.42	1.226

To determine the diffusion coefficient of a gas through a mixture of other gases, Reid and Sherwood (88) give the following equation:

$$D_{1,2,3,\ldots n} = \frac{1 - y_1}{y_2/D_{12} + y_3/D_{13} + y_4/D_{14} + \ldots}, \qquad (145)$$

where $\underline{D}_{1,2,3,\ldots\underline{n}}$ = the diffusion coefficient of component 1;

$\underline{y}_{\underline{n}}$ = the mole fraction of component $\underline{n}$; and

$\underline{D}_{1,\underline{n}}$ = the binary diffusion coefficient for two gases, 1 and $\underline{n}$.

Using this equation, the diffusion constant of chlorine dioxide through mixtures of chlorine, ozone, oxygen, and He were calculated according to the conditions of the experiments, Table XXXIII. Since the concentration of chlorine dioxide was considered very low its mole fraction is considered zero.

The ratio of these diffusion coefficients should give an indication of the change in rate of a reaction that is dependent on the rate of diffusion. Therefore, in Table XXXIV the ratio of the diffusion coefficients is compared with the ratio of the amount of product formed in the reaction. These ratios are within experimental error. However, this does not say that the reaction depends on diffusion controlled reactions, only that they could be happening.

TABLE XXXIII

DIFFUSION COEFFICIENTS OF ClO_2 THROUGH MIXTURES OF Cl_2, O_3, O_2, AND He AT 273°K AND OTHER EXPERIMENTAL CONDITIONS

$\underline{D}$, $cm.^2 sec.^{-1}$	Mole Fraction				Total Pressure, atm.
	Cl_2	O_3	He	O_2	
0.146	0.500	0.500	--	--	0.395
0.137	0.333	0.333	0.333	--	0.592
0.113	0.333	0.333	--	0.333	0.592

TABLE XXXIV

RATIO OF DIFFUSION COEFFICIENT COMPARED TO RATIO OF PRODUCT FORMED BASED ON SYSTEM WITHOUT DILUENT

System	Product Formed, moles ClO_4^- (10^4)	Diffusion Constant, $cm.^2 sec.^{-1}$	Ratio Based on Cl_2, O_3, ClO_2 System	
			ClO_4^-	$\underline{D}$
Cl_2, O_3	1.46 ± 0.14	0.146	1.0	1.0
Cl_2, O_3, He	1.30 ± 0.14	0.137	0.89	0.94
Cl_2, O_3, O_2	1.21 ± 0.14	0.113	0.83	0.77

DIFFUSION RATE OF O_3 INTO REACTION ZONE

Using the Lennard-Jones Force Constants found in Table XXX and Equations (143) and (144), the σ_{12}, $\underline{kT}/\varepsilon_{12}$, and $\Omega_{\underline{D}}$ were found for ozone diffusing through chlorine, as 3.92, 1.02, and 1.426. These were substituted into Equation (140) to give $\underline{PD}_{O_3,Cl_2} = 0.678$ $cm.^2 atm./sec.$

The reaction zone to be considered is the first 3 inches of the reactor having a diameter of 2 inches. The volume of this element is 155 $cm.^3$ The area through which the diffusion occurs is the area of a circle 2 inches in diameter or 20.3 $cm.^2$ The distance over which diffusion occurs is 7.62 cm.

From page 265 of Reid and Sherwood (88):

$$N_1 = \frac{-D_{12}\, P}{RT\, p_2} \frac{dp_1}{dZ} , \tag{146}$$

where N_1 = instantaneous flux, g.-moles/sec.cm.^{2};

P = total pressure, atm.;

p_1, p_2 = partial pressure of two components, atm.;

R = gas constant, cm.^{3}atm./g. mole °K;

T = temperature, °K; and

Z = distance of diffusion, cm.

Therefore, since

$$N_1\, dZ = \frac{-D_{12}\, P}{RT\, p_2}\, dp_1 \tag{147}$$

consider p_2 constant,

$$N_1 \int_{Z_1}^{Z_2} dZ = - \frac{D_{12}\, P}{RT\, p_2} \int_{p_{11}}^{p_{12}} dp_1 \tag{148}$$

integrate

$$N_1(Z_2 - Z_1) = - \frac{D_{12}\, P}{RT\, p_2} (p_{12} - p_{11}) \tag{149}$$

or

$$(p_{12} - p_{11}) = \frac{N_1(Z_2 - Z_1)\, RT\, p_2}{- D_{12}\, P} . \tag{150}$$

Therefore, Equation (150) gives the difference between the partial pressure of ozone outside the reaction zone, p_{11}, to that inside it, p_{12}.

The rate of reaction of ozone is proportional to the rate of formation of dichlorine heptoxide and can be estimated as at least seven times the rate of formation of dichlorine heptoxide. The rate of formation of dichlorine heptoxide is given in Table XVI as 1.31×10^{-8} moles/liter sec. when no diluent

is present, so that the rate of decomposition of ozone is at least 9.17×10^{-8} moles/liter sec. Therefore, 9.17×10^{-8} moles/liter sec. of ozone must diffuse into the element to counteract removal by reaction. The mass flux, $\underline{N}_1$, into the element is required to be

$$\underline{N}_1 = \frac{9.17 \times 10^{-8} \text{ moles/liter sec.}}{1000 \text{ cm.}^3\text{/liter}} \times \frac{155 \text{ cm.}^3}{20.3 \text{ cm.}^2} = 7.01 \times 10^{-10} \text{ moles/cm.}^2\text{sec.}$$

$\underline{R}$ = 82.06 cm.^{3}atm./g.-mole °K

$\underline{T}$ = 273°K.

$\underline{Z}_2$ = 7.62 cm.; $\underline{Z}_1$ = 0

$\underline{p}_2$ = 150/760

$\underline{p}_{11}$ = 150/760

$\underline{D}_{12}\,\underline{P}$ = 0.0678 cm.^{2}atm./sec.

Therefore,

$$p_{12} = p_{11} - \frac{N_1 Z_2 RT p_2}{D_{12} P} \qquad (151)$$

$$p_{12} = \frac{150}{760} - \frac{(7.01 \times 10^{-10})(7.62)(82.06)(273)(150/760)}{0.0678}$$

$$p_{12} = 197.5 \times 10^{-3} - 0.348 \times 10^{-3}.$$

Therefore, the difference in partial pressure is negligible and the diffusion of ozone into the reaction zone is not a rate-controlling step.

APPENDIX XII

METHOD OF CALCULATION AND SAMPLE CALCULATIONS FOR ATTAINMENT OF RATE CONSTANTS

METHOD OF DETERMINING RATE CONSTANTS

Equation (130) is the basic equation for the system under study. When Equations (133), (134), and (135) are substituted for Equation (97) the following is obtained:

$$\frac{d\,[Cl_2O_7]}{dt} = \frac{(ABC)\, I_{abs}}{ABC + 2k_{100}[Cl][Cl_2] + 2k_{102}[Cl][O_2] + 2k_{101}[Cl][He] + k_{74}} \qquad (152)$$

where $\underline{ABC} = \underline{k}_{135}[O_3][\underline{M}'] + \underline{k}_{133}[O_3][O_2] + \underline{k}_{134}[O_3][He]$.

The rate constants $\underline{k}_{135}$, $\underline{k}_{133}$, and $\underline{k}_{134}$ are unknown while $\underline{k}_{100}$, $\underline{k}_{101}$, $\underline{k}_{102}$, and $\underline{k}_{74}$ are known or can be estimated from the literature. The rate constant $\underline{k}_{100}$ was estimated to be 2.0×10^{10} liter^2/mole^{2}sec. at 20°C. from the data of Hutton and Wright (25). Hutton and Wright also give 4.25×10^9 liter^2/mole^{2}sec. at 20°C. for the rate constant of chlorine atom recombination due to argon. It has been assumed that this is an acceptable value for $\underline{k}_{101}$, the rate constant of chlorine atom recombination due to helium. Ashmore, et al. (81) have reported a surface recombination coefficient, $\gamma = 1 \times 10^{-4}$, for chlorine atoms on a water washed "pyrex" surface. Using Equation (153),

$$\gamma = \frac{4kV}{\bar{v}S}, \qquad (153)$$

where $\underline{k}$ = first order rate constant, sec.$^{-1}$;

$\underline{V}$ = volume of reaction zone, 155 cc.;

$\underline{\bar{v}}$ = mean atom velocity at 0°C., 4.04×10^4 cm./sec.; and

$\underline{S}$ = surface area of reaction zone, 142.3 cm.^{2};

given by Herron (90), k_{74} for the recombination of chlorine atoms on the surface of the reactor at 0°C. was calculated as 0.93 $sec.^{-1}$. The rate constant for Equation (102),

$$2\ Cl + O_2 \longrightarrow Cl_2 + O_2, \tag{102}$$

was estimated from the data of Johnston, et al. (35). Equations (77) through (81) of Johnston, et al. represent recombination of chlorine atoms due to oxygen under the conditions studied in this work. These five equations can be reduced to Equation (81),

$$Cl + ClOO \longrightarrow Cl_2 + O_2, \tag{81}$$

whose rate of chlorine atom disappearance can be written as

$$\frac{-d\,[Cl]}{dt} = k_{81}[Cl][ClOO]. \tag{154}$$

Also from Johnston, et al. the concentration of ClOO can be written as

$$[ClOO] = K_1[Cl][O_2]. \tag{155}$$

Therefore, Equation (155) can be substituted into Equation (154) to give Equation (156),

$$\frac{-d\,[Cl]}{dt} = k_{81}\,K_1[Cl]^2[O_2], \tag{156}$$

which is the desired form of the equation. Therefore, k_{102} should equal $k_{81}\,K_1$. Johnston, et al. give K_1 as 2.18 liters/mole and k_{81} as 9.39×10^{10} liter/mole sec. at 25°C. Therefore, k_{102} is equal to 2.05×10^{11} $liters^2/mole^2 sec.$ at 25°C. These rate constants are those given in Table XVIII and are used in the following calculations despite the fact that k_{100}, k_{101}, and k_{102} are determined at the

wrong temperature. No adjustment was made to these rate constants to account for the temperature difference because of the seeming lack of temperature dependence within the system, and the lack of temperature dependence information about the rate constants.

In the following calculations two basic equations were used, Equation (152) and Equation (157),

$$2I_{abs} = k_{135}[O_3][M'][Cl] + k_{133}[O_3][O_2][Cl] + k_{134}[O_3][He][Cl] + 2k_{100}[Cl]^2[Cl_2] + 2k_{102}[Cl]^2[O_2] + 2k_{101}[Cl]^2[He] + k_{74}[Cl]. \quad (157)$$

Estimates of $\underline{k}_{133}$, $\underline{k}_{134}$, and $\underline{k}_{135}$ were then made using a trial and error procedure based on the average rate of formation of dichlorine heptoxide given in Table XVI.

First, the system containing only chlorine and ozone was considered at zero time. Since no oxygen or helium was present, the only unknowns in Equation (157) were $\underline{k}_{135}$ and the chlorine atom concentration. The rate constant, $\underline{k}_{135}$, was then arbitrarily set and the chlorine atom concentration calculated. These two values were then used to calculate the instantaneous rate of dichlorine heptoxide formation at zero time using Equation (152). This procedure was followed several times until the instantaneous rate of dichlorine heptoxide formation at zero time was numerically similar to the average rate of formation of dichlorine heptoxide given in Table XVI for the system with no diluent.

The system containing only chlorine and ozone at the start was then considered after ten hours of reaction time. The amount of ozone, chlorine, and oxygen present in the system was based on the amount of dichlorine heptoxide formed and the total pressure rise. Because of the presence of oxygen, an

estimate had to be made for $\underline{k}_{133}$. Using the best $\underline{k}_{135}$ found in the first procedure, $\underline{k}_{133}$ could be estimated and the chlorine atom concentration determined using Equation (157). These values were then substituted into Equation (152) and the instantaneous rate of formation of dichlorine heptoxide at 10 hours calculated. The estimates of $\underline{k}_{133}$ and $\underline{k}_{135}$ were then further refined so that the average of the instantaneous rates at zero time and 10 hours was approximately equal to the average rate of formation of dichlorine heptoxide given in Table XVI.

Further refinement of $\underline{k}_{133}$ and $\underline{k}_{135}$ was made by applying them to the reaction system where oxygen was used as the diluent. Again the average of the instantaneous rates at zero time and 10 hours was balanced against the reported average for the system in Table XVI.

Finally, $\underline{k}_{134}$ was estimated using the same process for the chlorine, ozone, helium reaction system.

The accepted values for $\underline{k}_{133}$, $\underline{k}_{134}$, and $\underline{k}_{135}$ based on the reaction zone of 0.155 liter at 0°C. are given in Table XVIII.

SAMPLE CALCULATIONS FOR DETERMINING RATE CONSTANTS

The following will give sample calculations for the above procedures.

The calculation of $\underline{k}_{74}$ was done in the following manner. The reaction zone is considered to be a cylinder 2 inches in diameter and 3-inches long with one open end.

$V = \pi r^2 h + 3.14(1 \text{ in.})^2(3 \text{ in.})\ (2.54 \text{ cm./in.})^3 = 155 \text{ cm.}^3$

$S = \pi r^2 + \pi Dh = 3.14(1 \text{ in.})^2(2.54 \text{ cm./in.})^2 + 3.14(2 \text{ in.})(3 \text{ in.})(2.54 \text{ cm./in.})^2$

$= 142.3 \text{ cm.}^2$

$\bar{v} = (8RT/\pi h)^{1/2} = [(8)(8.314 \times 10^7 \text{ ergs/deg. mole})(273°K)/3.14(35.457 \text{ g./mole})]^{1/2}$

$= 4.04 \times 10^4 \text{ cm./sec.}$

From Equation (153),

$$k_{74} \text{ at } 0°C. = \frac{\gamma \bar{v} S}{4V} = \frac{(1 \times 10^4)(4.04 \times 10^4 \text{ cm./sec.})(142.3 \text{ cm.}^2)}{(4)(155 \text{ cm.}^3)}$$

$$= 0.93 \text{ sec.}^{-1}$$

For the attainment of rate constants and chlorine atom concentrations calculations similar to those below were used.

Conditions: 0 time at 0°C.

Reactant concentrations: $[O_3] = [Cl_2] = 8.82 \times 10^{-3}$ moles/liter.

Rate constants as shown in Table XVIII.

Light intensity: 3.05×10^{15} quanta/sec.

From Equation (157)

$$2I_{abs} = k_{135}[O_3][M'][Cl] + 2k_{100}[Cl]^2[Cl_2] + k_{74}[Cl]$$

where

$$2I = \frac{2(3.05 \times 10^{15} \text{ quanta/sec.})(1 \text{ molecule/quanta})}{(0.155 \text{ liter})(6.023 \times 10^{23} \text{ molecules/mole})} = 6.54 \times 10^{-8} \text{ moles/liter sec.}$$

therefore,

$$6.54 \times 10^{-8} \text{ moles/liter sec.} = (2.2 \times 10^{4} \text{ liter}^2/\text{mole}^2\text{sec.})(8.82 \times 10^{-3} \text{ moles/liter})(17.6 \times 10^{-3} \text{ moles/liter})[Cl] + 2(2.0 \times 10^{10} \text{ liter}^2/\text{mole}^2\text{sec.})(8.82 \times 10^{-3} \text{ moles/liter})[Cl]^2 + 0.93 \text{ sec.}^{-1}[Cl]$$

$$6.54 \times 10^{-8} = 3.42[Cl] + 3.53 \times 10^{8}[Cl]^2 + 0.93[Cl]$$

$$[Cl] = 8.78 \times 10^{-9} \text{ moles/liter.}$$

From Equation (152)

$$\frac{d[Cl_2O_7]}{dt} = \frac{(k_{135}[O_3][M'])\ (I_{abs})}{k_{135}[O_3][M'] + 2k_{100}[Cl_2][Cl] + k_{74}}$$

$$= \frac{(3.42)(3.27 \times 10^{-8})}{3.42 + 3.10 + 0.93}$$

$$= 1.50 \times 10^{-8} \text{ moles/liter sec.}$$

Since

$$\phi_{Cl_2O_7} = \frac{d[Cl_2O_7]}{dt} \Big/ I_{abs}$$

$$= \frac{1.50 \times 10^{-8}}{3.27 \times 10^{-8}} = 0.459.$$

METHOD OF DETERMINING SERIES OF REACTION RATES AND QUANTUM YIELDS

With the appropriate rate constants set, a series of calculations were made to determine if a curve similar to actual data could be obtained. The results of these calculations are given in Table XIX and Fig. 15. The method of calculation was done in the following manner: Starting at zero time, an instantaneous rate was calculated using Equations (152) and (157). This calculated rate was then assumed to be constant for the first 0.5 hour of the reaction. The amount of Cl_2O_7 formed could be calculated and, based on the

Cl_2O_7 formed, new concentrations of O_3, Cl_2, and O_2 calculated. The concentration of He remains constant. The new concentrations of O_3, Cl_2, and O_2 were based on 7 moles of O_3 destroyed and 7 moles of O_2 formed for each mole of Cl_2O_7 formed and one mole of Cl_2 disappearing for each mole of Cl_2O_7 formed. Using these new concentrations the instantaneous rate of formation of Cl_2O_7 was calculated at 0.5 hour. This new rate was then used to determine the amount of Cl_2O_7 formed in the next 0.5 hour and was added to the amount formed in the first 0.5 hour to give the total Cl_2O_7 formed in the first hour. The instantaneous rate at one hour could then be calculated based on the new concentrations of Cl_2, O_3, and O_2. And the process continued to give calculated data at 2, 4, 7, 10, 15, 20, and 26 hours.

RESULTS OF CALCULATIONS WHEN THE ENTIRE VOLUME OF THE REACTOR IS CONSIDERED THE REACTION ZONE

In the previous calculations the reaction zone was considered to be the front portion of the reactor (0.155 liter) where the light beam first enters and where it is almost entirely absorbed. For this reason the concentrations of chlorine atom and the rate of formation of Cl_2O_7 is based on 0.155 liter. If, however, the entire volume of the reactor (0.6116 liter) is used for the calculations the rate constants, $\underline{k}_{74}$, $\underline{k}_{133}$, and $\underline{k}_{135}$ are changed to 0.80 $sec.^{-1}$, 2.5×10^4 $liter^2/mole^2sec.$, and 1.2×10^4 $liter^2/mole^2sec$. The rate constant, $\underline{k}_{134}$, remains less than 1.0×10^2 $liter^2/mole^2sec$. The rate constants, $\underline{k}_{133}$ and $\underline{k}_{135}$, are decreased because the chlorine atom concentration is now based on a greater volume and is decreased. The rate constant $\underline{k}_{74}$ is decreased because of a change in the surface-to-volume ratio considered.

If the above rate constants are used to make a series of calculations as previously described, the results are very similar to those using a reaction zone of 0.155 liter and are given in Table XXXV and Table XXXVI.

TABLE XXXV

INSTANTANEOUS REACTION RATES AND QUANTUM YIELDS AT 0°C.
BASED ON ENTIRE VOLUME OF THE REACTOR

Time, hr.	Species Concentration, moles/liter						ClO_4^- Formed, moles x 10^4	Reaction Rate, moles/liter sec. x 10^9	Quantum Yield of Cl_2O_7 Formation
	O_3 x 10^3	Cl_2 x 10^3	He x 10^3	O_2 x 10^4	Cl x 10^9	Cl_2O_7 x 10^4			
				Helium as Diluent					
0	8.82	8.82	8.82	0	3.85	0	0	3.58	0.432
$\frac{1}{2}$	8.77	8.81	8.82	0.452	3.81	0.065	0.079	3.55	0.428
1	8.73	8.81	8.82	0.896	3.78	0.128	0.157	3.49	0.420
2	8.64	8.79	8.82	1.78	3.70	0.254	0.311	3.40	0.409
4	8.47	8.77	8.82	3.49	3.57	0.499	0.611	3.26	0.392
7	8.22	8.74	8.82	5.96	3.40	0.851	1.04	3.07	0.371
10	7.99	8.70	8.82	8.27	3.28	1.18	1.45	2.89	0.349
15	7.63	8.65	8.82	11.9	3.11	1.70	2.08	2.66	0.321
20	7.29	8.60	8.82	15.3	2.98	2.18	2.67	2.48	0.299
26	6.92	8.55	8.82	19.0	2.85	2.72	3.32	2.31	0.278
				No Diluent					
0	8.82	8.82	0	0	4.06	0	0	3.77	0.455
10	7.71	8.73	0	12.9	3.12	1.19[a]	1.46±0.14[a]	2.77	0.333
				O_2 as Diluent					
0	8.82	8.82	0	88.2	1.55	0	0	2.94	0.354
10	7.94	8.76	0	98.8	1.51	0.99[a]	1.21±0.14[a]	2.68	0.323

[a]These are actual experimental values not from calculations.

TABLE XXXVI

PERCENTAGE OF LIGHT ENERGY ABSORBED USED BY DIFFERENT EQUATIONS BASED ON ENTIRE VOLUME OF REACTOR

Time, hr.	Effect of Indicated Reaction, %					
	(135)	(133)	(100)	(102)	(101)	(74)
			O_3, Cl_2, He System			
0	43.2	0	31.6	0	6.7	18.6
1	41.6	0.4	30.2	3.2	6.4	18.2
2	40.1	0.9	29.0	6.0	6.2	17.8
4	37.6	1.6	26.9	10.9	5.8	17.2
7	34.5	2.5	24.4	17.1	5.1	16.4
10	31.6	3.3	22.6	21.9	4.8	15.8
15	27.9	4.2	20.2	28.4	4.4	14.9
20	24.9	5.0	18.4	33.5	3.9	14.3
26	22.2	5.6	16.7	38.1	3.6	13.8
			O_3, Cl_2 System			
0	45.5	0	35.0	0	--	19.5
10	28.6	4.7	20.5	31.1	--	15.1
			O_3, Cl_2, O_2 System			
0	17.3	18.1	5.1	52.1	--	7.4
10	14.5	17.8	4.8	55.6	--	7.3

APPENDIX XIII

CALCULATION OF ClO CONCENTRATION AFTER 10 HOURS IN O_3, Cl_2, He SYSTEM AND O_3, Cl_2, O_2 SYSTEM

From Johnston, et al. (35),

$$[ClO] = [Cl]\sqrt{K_1K_2[O_2]}, \qquad (158)$$

where $K_1 = 2.18$ liter/mole

$K_2 = 227$ liter/mole.

From Table XVIII at 10 hours,

O_3, Cl_2, He System	O_3, Cl_2, O_2 System
$[Cl] = 6.91 \times 10^{-9}$	$[Cl] = 3.07 \times 10^{-9}$
$[O_2] = 8.25 \times 10^{-4}$	$[O_2] = 9.88 \times 10^{-3}$

Therefore for the O_3, Cl_2, He system,

$$[ClO] = (6.91 \times 10^{-9})\sqrt{2.18(227)(8.25 \times 10^{-4})}$$

$$= 6.91 \times 10^{-9}\sqrt{40.8 \times 10^{-2}}$$

$$= 6.91 \times 10^{-9}\,(6.39 \times 10^{-1})$$

$$[ClO] = 4.22 \times 10^{-9} \text{ moles/liter.}$$

For the O_3, Cl_2, O_2 system,

$$[ClO] = 3.07 \times 10^{-9}\sqrt{(2.18)(227)(9.88 \times 10^{-3})}$$

$$= 3.07 \times 10^{-9}\sqrt{4.89}$$

$$= 3.07 \times 10^{-9}\,(2.21)$$

$$[ClO] = 6.78 \times 10^{-9} \text{ moles/liter.}$$

Since the concentration of chlorine atoms used is based on the reaction zone of 0.155 liter, the calculated ClO concentration is based on this volume. The concentration of ClO outside of the reaction zone is probably negligible.

APPENDIX XIV

TABULATION OF DATA FOR EACH RUN

Table XXXVII presents a tabulation of the data for each experimental run. The moles of product given is converted from equivalents in the case of hypochlorite and chlorate. The amount of chlorite formed was negligible so this does not appear. Chloride was not determined so this does not appear. Under the column "Sample," CCl_4-E stands for CCl_4-extraction material; WW, water wash material; 0.1N NaOH, 0.1N NaOH material; and RR, reactor rinse material.

TABLE XXXVII

DATA FOR EACH EXPERIMENTAL RUN

Run	Temp., °C.	Time of Run, hr.	Moles (10^3) of Reactant Pressure, mm. Hg						Light Intensity, quanta/sec. (10^{-15})	Sample	Moles (10^3) of Ionic Species Found		
			O_3	Cl_2	He	O_2	Initial	Final			ClO^-	ClO_3^-	ClO_4^-
1	-10.5	8.0	5.61	5.59	5.61	0.0	449.0	460.8	3.48	CCl_4-E	0.627	0.0089	0.131
										RR	0.0032	0.0003	0.000
										0.1N NaOH	4.12	0.052	0.000
2	-10.5	8.0	5.67	5.59	5.54	0.0	448.7	456.5	3.65	CCl_4-E	0.762	0.0123	0.153
										RR	0.0052	0.0004	0.000
										0.1N NaOH	4.08	0.048	0.000
3	-10.5	8.0	5.58	5.57	0.0	5.63	450.5	454.6	3.68	CCl_4-E	0.593	0.0051	0.050
										RR	0.0042	0.0008	0.000
										0.1N NaOH	4.59	0.042	0.000
4	-10.5	8.0	5.62	5.59	0.0	0.0	299.5	302.5	3.19	CCl_4-E	0.495	0.0047	0.000
										RR	0.0039	0.0004	0.0538
										0.1N NaOH	4.87	0.079	0.000
5	-10.5	4.0	5.60	5.55	5.64	0.0	449.0	448.9	3.15	CCl_4-E	0.627	0.0088	0.000
										RR	0.0201	0.0004	0.004
										0.1N NaOH	4.52	0.094	0.000
6	-10.5	20.0	5.60	5.58	5.65	0.0	450.5	447.8	3.12	CCl_4-E	0.451	0.0153	0.278
										RR	0.0108	0.0005	0.0195
										0.1N NaOH	N.D.[a]	0.0367	0.000
7	-10.5	4.0	4.61	5.59	6.64	0.0	450.4	449.8	2.83	CCl_4-E	0.622	0.0026	0.0463
										RR	0.0099	0.0004	0.0285
										0.1N NaOH	N.D.	0.0458	0.000

TABLE XXXVII (Continued)

DATA FOR EACH EXPERIMENTAL RUN

Run	Temp., °C.	Time of Run, hr.	Moles (10^3) of Reactant				Pressure, mm. Hg		Light Intensity, quanta/sec. (10^{-15})	Sample	Moles (10^3) of Ionic Species Found		
			O_3	Cl_2	He	O_2	Initial	Final			ClO^-	ClO_3^-	ClO_4^-
8	-10.5	14.0	5.61	5.59	5.60	0.0	449.3	452.9	3.09	CCl_4-E	0.607	0.0076	0.209
										RR	0.034	0.0004	0.041
										0.1N NaOH	N.D.	0.0392	0.000
9	-10.5	4.0	5.30	5.58	5.93	0.0	449.8	451.3	2.95	CCl_4-E	0.524	0.0028	0.000
										RR	0.0229	0.000	0.0352
										0.1N NaOH	N.D.	0.0462	0.000
10	-10.5	20.0	5.62	5.58	5.61	0.0	449.8	--	3.06	CCl_4-E	0.425	0.0194	0.288
										RR	0.004	0.0004	0.0150
										0.1N NaOH	N.D.	0.0308	0.000
11	-10.5	14.0	5.61	5.58	5.63	0.0	449.5	451.4	3.11	CCl_4-E	0.296	0.0086	0.1915
										RR	0.0056	0.0005	0.0354
										0.1N NaOH	N.D.	0.120	0.000
12	-10.5	4.0	5.61	5.59	5.58	0.0	449.2	448.6	3.04	CCl_4-E	0.339	0.0027	0.0575
										RR	0.0308	0.000	0.0732
										0.1N NaOH	N.D.	0.0791	0.000
13	-10.5	26.0	5.61	5.61	5.60	0.0	449.5	455.0	2.76	CCl_4-E	0.209	0.0083	0.285
										RR	0.008	0.0004	0.0345
										0.1N NaOH	N.D.	0.0254	N.D.
14	-10.5		5.61	5.60	5.60	0.0	449.5	--	3.12	Discontinued because of Refrigeration failure			
15	-10.5	4.0	5.61	5.60	5.59	0.0	450.0	449.8	2.41	CCl_4-E	0.291	0.0023	0.000
										RR	0.0254	0.0004	0.0806
										0.1N NaOH	N.D.	0.0513	N.D.

TABLE XXXVII (Continued)

DATA FOR EACH EXPERIMENTAL RUN

Run	Temp., °C.	Time of Run, hr.	Moles (10^3) of Reactant Pressure, mm. Hg O_3	Cl_2	He	O_2	Initial	Final	Light Intensity, quanta/sec. (10^{-15})	Sample	Moles (10^3) of Ionic Species Found ClO^-	ClO_3^-	ClO_4^-
16	-10.5	Never started because of film found on surface of reactor											
17	-10.5	4.0	5.60	5.59	5.61	0.0	450.5	449.4	2.20	CCl_4-E	0.310	0.0023	0.005
										RR	0.0060	0.000	0.0335
										0.1N NaOH	N.D.	0.1188	0.000
18	-10.5	Run never started because of problem with ozonizer											
19	-10.5	Run never started because of failure in distribution valve to pressure transducer											
20	0.0	4.0	5.39	5.39	5.40	0.0	450.3	449.5	2.27	CCl_4-E	0.256	0.0023	0.000
										RR	0.0099	0.0005	0.0515
										0.1N NaOH	N.D.	0.05050	N.D.
21	0.0	7.0	5.45	5.36	5.31	0.0	449.1	448.1	2.05	CCl_4-E	0.296	0.0023	0.0005
										RR	0.0034	0.0004	0.0615
										0.1N NaOH	N.D.	0.0462	N.D.
22	0.0	7.0	5.39	5.38	5.42	0.0	450.3	450.8	2.96	CCl_4-E	0.229	0.0023	0.005
										RR	0.0031	0.000	0.0435
										0.1N NaOH	N.D.	0.0267	N.D.
23	0.0	4.0	5.41	5.37	5.37	0.0	449.9	449.4	3.23	CCl_4-E	0.244	0.0026	0.000
										RR	0.0113	0.0005	0.0405
										0.1N NaOH	N.D.	0.1008	N.D.
24	0.0	10.0	5.39	5.39	5.36	0.0	448.9	452.3	3.46	CCl_4-E	0.290	0.0026	0.1025
										RR	0.0275	0.0005	0.0480
										0.1N NaOH	N.D.	0.0358	N.D.

TABLE XXXVII (Continued)

DATA FOR EACH EXPERIMENTAL RUN

Run	Temp., °C.	Time of Run, hr.	Moles (10^3) of Reactant Pressure, mm. Hg						Light Intensity, quanta/sec. (10^{-15})	Sample	Moles (10^3) of Ionic Species Found		
			O_3	Cl_2	He	O_2	Initial	Final			ClO^-	ClO_3^-	ClO_4^-
25	0.0	20.0	5.41	5.36	5.37	0.0	449.9	455.0	3.33	CCl_4-E	0.154	0.0064	0.2713
										RR	0.0159	0.000	0.0900
										0.1N NaOH	N.D.	0.0208	N.D.
26	0.0	15.0	5.39	5.38	5.57	0.0	455.0	451.6	3.44	CCl_4-E	0.287	0.0039	0.1813
										RR	0.0051	0.000	0.0625
										0.1N NaOH	N.D.	0.0396	N.D.
27	0.0	7.0	5.39	5.39	5.33	0.0	448.3	449.3	3.28	CCl_4-E	0.259	0.0023	0.005
										RR	0.004	0.0004	0.0985
										0.1N NaOH	N.D.	0.0363	N.D.
28	0.0	10.0	5.43	5.39	5.32	0.0	448.2	451.1	3.23	CCl_4-E	0.437	0.0025	0.0188
										RR	0.0051	0.0005	0.1125
										0.1N NaOH	N.D.	0.0800	N.D.
29	0.0	10.0	3.32	5.38	7.45	0.0	450.0	451.3	3.46	CCl_4-E	0.490	0.0027	0.0475
										RR	0.0082	0.000	0.1115
										0.1N NaOH	N.D.	0.0308	N.D.
30	0.0	10.0	10.5	5.4	0.262	0.0	449.8	452.5	3.34	CCl_4-E	0.577	0.0101	0.0100
										RR	0.0218	0.0004	0.155
										0.1N NaOH	N.D.	0.0641	N.D.
31	0.0	10.0	5.34	0.0	10.7	0.0	448.5	469.7	1.52	CCl_4-E	0.003	0.000	0.000
										RR	0.0009	0.0005	0.000
										0.1N NaOH	N.D.	0.0017	N.D.

TABLE XXXVII (Continued)

DATA FOR EACH EXPERIMENTAL RUN

Run	Temp., °C.	Time of Run, hr.	Moles (10^3) of Reactant				Pressure, mm. Hg		Light Intensity, quanta/sec. (10^{-15})	Sample	Moles (10^3) of Ionic Species Found		
			O_3	Cl_2	He	O_2	Initial	Final			ClO^-	ClO_3^-	ClO_4^-
32	0.0	10.0	3.82	0.0	12.3	0.0	449.5	451.2	1.73	WW	0.003	0.0006	0.000
										RR	0.000	0.000	0.000
										0.1N NaOH	N.D.	0.0011	N.D.
33	0.0	10.0	5.47	5.39	5.26	0.0	449.1	446.5	1.65	WW	0.731	0.0031	0.0025
										RR	0.006	0.0004	0.0625
										0.1N NaOH	N.D.	0.1140	0.000
34	0.0	10.0	7.44	5.38	3.39	0.0	451.5	450.7	1.91	WW	0.681	0.0027	0.005
										RR	0.0053	0.000	0.0733
										0.1N NaOH	N.D.	0.133	0.000
35	0.0	10.0	10.79	5.33	0.0	0.0	449.0	451.1	2.16	WW	0.828	0.0033	0.000
										RR	0.0062	0.0004	0.112
										0.1N NaOH	N.D.	0.1715	0.000
36	0.0	10.0	5.40	5.39	5.38	0.0	450.0	448.9	1.99	WW	0.656	0.0026	0.005
										RR	0.004	0.000	0.0775
										0.1N NaOH	N.D.	0.0804	0.000
37	0.0	10.0	10.78	5.38	0.0	0.0	450.0	456.5	1.96	WW	0.500	0.0028	0.0110
										RR	0.0418	0.0005	0.0568
										0.1N NaOH	N.D.	0.1145	0.000
38	0.0	Run never started because of failure of refrigeration system											
39	0.0	10.0	5.42	5.38	5.36	0.0	448.9	455.1	3.94	WW	0.577	0.0023	0.0538
										RR	0.0229	0.0004	0.1373
										0.1N NaOH	N.D.	0.0583	0.000

TABLE XXXVII (Continued)

DATA FOR EACH EXPERIMENTAL RUN

Run	Temp., °C.	Time of Run, hr.	Moles (10^3) of Reactant				Pressure, mm. Hg		Light Intensity, quanta/sec. (10^{-15})	Sample	Moles (10^3) of Ionic Species Found		
			O_3	Cl_2	He	O_2	Initial	Final			ClO^-	ClO_2^-	ClO_4^-
40	0.0	10.0	5.38	5.37	0.0	0.0	299.5	307.2	3.65	WW	0.567	0.0031	0.0038
										RR	0.0066	0.0005	0.1694
										0.1N NaOH	N.D.	0.0958	0.000
41	0.0	10.0	5.39	5.38	0.0	0.0	300.7	308.5	4.196	WW	0.692	0.0027	0.0219
										RR	0.0052	0.0004	0.1791
										0.1N NaOH	N.D.	0.0832	0.000
42	0.0	10.0	5.42	5.38	0.0	5.53	454.4	459.4	4.27	WW	0.449	0.0023	0.0375
										RR	0.004	0.000	0.1464
										0.1N NaOH	N.D.	0.0675	0.000
43	0.0	10.0	5.38	5.39	0.0	5.38	450.1	456.3	4.39	WW	0.582	0.0025	0.0150
										RR	0.0035	0.000	0.144
										0.1N NaOH	N.D.	0.0750	0.000
44	0.0	10.0	3.59	5.37	7.18	0.0	449.5	453.0	4.43	WW	0.418	0.0027	0.0369
										RR	0.0048	0.0005	0.1388
										0.1N NaOH	N.D.	0.0342	0.000
45	0.0	10.0	8.99	5.37	1.79	0.0	448.9	460.2	4.39	WW	0.519	0.0027	0.0734
										RR	0.0069	0.0005	0.1388
										0.1N NaOH	N.D.	0.1007	0.000
46	0.0	20.0	5.40	5.39	5.43	0.0	451.9	460.1	4.19	WW	0.465	0.0034	0.2306
										RR	0.001	0.0004	0.1928
										0.1N NaOH	N.D.	0.0507	0.000

TABLE XXXVII (Continued)

DATA FOR EACH EXPERIMENTAL RUN

Run	Temp., °C.	Time of Run, hr.	Moles (10^3) of Reactant				Pressure, mm. Hg		Light Intensity, quanta/sec. (10^{-15})	Sample	Moles (10^3) of Ionic Species Found		
			O_3	Cl_2	He	O_2	Initial	Final			ClO^-	ClO_3^-	ClO_4^-
47	0.0	15.0	5.42	5.38	5.34	0.0	449.6	456.8	4.27	WW	0.457	0.0028	0.0469
										RR	0.004	0.0005	0.2853
										0.1N NaOH	N.D.	0.0563	0.000
48	0.0	26.0	5.38	5.38	5.38	0.0	449.5	454.7	4.19	WW	0.534	0.0045	0.1431
										RR	0.004	0.0005	0.3678
										0.1N NaOH	N.D.	0.0441	0.000
49	0.0	4.0	5.39	5.39	5.37	0.0	449.5	448.8	3.89	WW	0.505	0.0031	0.035
										RR	0.004	0.0005	0.0991
										0.1N NaOH	N.D.	0.115	0.000
50	0.0	7.0	5.39	5.39	5.38	0.0	449.3	450.4	3.62	WW	0.529	0.0024	0.000
										RR	0.0049	0.000	0.1718
										0.1N NaOH	N.D.	0.1015	0.000

[a] N.D. = Not Determined.